AFRL-ML-WP-TR-2003-4173

AIR VEHICLE TECHNOLOGY INTEGRATION PROGRAM (AVTIP)

Delivery Order 0004: Advanced Sol-Gel Adhesion Processes

Kay Y. Blohowiak
Robert A. Anderson
Ronald R. Stephenson
Kristina S. Preedy

The Boeing Company, Phantom Works
P.O. Box 3999, M/S 73-09
Seattle, WA 98124-2499

APRIL 2002

Final Report for 01 February 2001 – 31 March 2002

Approved for public release; distribution is unlimited.

STINFO FINAL REPORT

MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750

NOTICE

USING GOVERNMENT DRAWINGS, SPECIFICATIONS, OR OTHER DATA INCLUDED IN THIS DOCUMENT FOR ANY PURPOSE OTHER THAN GOVERNMENT PROCUREMENT DOES NOT IN ANY WAY OBLIGATE THE U.S. GOVERNMENT. THE FACT THAT THE GOVERNMENT FORMULATED OR SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA DOES NOT LICENSE THE HOLDER OR ANY OTHER PERSON OR CORPORATION; OR CONVEY ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE, OR SELL ANY PATENTED INVENTION THAT MAY RELATE TO THEM.

THIS REPORT HAS BEEN REVIEWED BY THE OFFICE OF PUBLIC AFFAIRS (ASC/PA) AND IS RELEASABLE TO THE NATIONAL TECHNICAL INFORMATION SERVICE (NTIS). AT NTIS, IT WILL BE AVAILABLE TO THE GENERAL PUBLIC, INCLUDING FOREIGN NATIONS.

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

/s/

JAMES MAZZA
Team Lead
Adhesives, Composites & Elastomers Team
Materials Integrity Branch

/s/

MARY ANN PHILLIPS
Chief
Materials Integrity Branch
Materials & Manufacturing Directorate

/s/

GARY KEPPLE
Deputy Chief
Systems Support Division
Materials & Manufacturing Directorate

Do not return copies of this report unless contractual obligations or notice on a specific document require its return.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*
April 2002

2. REPORT TYPE
Final

3. DATES COVERED *(From - To)*
02/01/2001 – 03/31/2002

4. TITLE AND SUBTITLE
AIR VEHICLE TECHNOLOGY INTEGRATION PROGRAM (AVTIP)
Delivery Order 0004: Advanced Sol-Gel Adhesion Processes

5a. CONTRACT NUMBER
F33615-00-D-3052

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
63716D

5d. PROJECT NUMBER
2401

5e. TASK NUMBER
00

5f. WORK UNIT NUMBER
TM

6. AUTHOR(S)
Kay Y. Blohowiak
Robert A. Anderson
Ronald R. Stephenson
Kristina S. Preedy

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The Boeing Company, Phantom Works
P.O. Box 3999, M/S 73-09
Seattle, WA 98124-2499

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Materials and Manufacturing Directorate
Air Force Research Laboratory
Air Force Materiel Command
Wright-Patterson AFB, OH 45433-7750

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/MLSA

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-ML-WP-TR-2003-4173

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
Report contains color.

14. ABSTRACT
This report summarizes optimization work for surface preparations and hybrid primers utilizing sol-gel technology on metal alloy substrates. The project focuses on the development and optimization of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure and 350°F-cure epoxy adhesives. Several improvements to the Boegel-EPII materials and processes were identified in this work. For example, addition of a surfactant can improve the appearance and uniformity of the sol-gel coatings, but is not critical for achieving good performance on these alloys.

Studies indicate that careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Under carefully controlled laboratory conditions, it is possible to yield good performance for many of the abrasive media, but when subjected to conditions that mimic a repair scenario, only a few of the abrasive media gave reproducible performance. Surface contamination on the metal was a result of smeared adhesive, overheating of the abrasive pad or tool, or unacceptable cleaning of the surface. Performance using downselected abrasive media and tools was verified using hot/wet testing, such as the wedge test and double cantilever beam testing. Procedures were documented specifying all of the preferred materials and processes.

15. SUBJECT TERMS
sol-gel, adhesive bonding, surface preparation, repair, adhesives

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT:	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON (Monitor) / 19b. TELEPHONE NUMBER *(Include Area Code)*
Unclassified	Unclassified	Unclassified	SAR	80	James Mazza (937) 255-7778

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

Table of Contents

List of Figures

List of Tables

ACKNOWLEDGEMENTS:

The Boeing Company is pleased to be part of a Tri-Services/Industry working team developing technology under Strategic Environmental Research and Development Program (SERDP) Project PP-1113. The Boeing Company leads the sol-gel development and technical integration associated with this effort under Air Force contract F33615-00-D-3052, Delivery Order #4. This report encompasses work performed between February 2001 and March 2002. We would like to acknowledge Valerie Loebs and Gene Ledbury of Boeing Phantom Works for their contribution to surface analysis work, and Jake Grob for sample preparation and data management. In addition, we would like to acknowledge our SERDP team members and our colleagues from Boeing Commercial Airplanes for collaborative discussions and contributions to the overall effort.

1 Executive Summary

This report summarizes the continuing efforts of the Strategic Environmental Research and Development Program (SERDP) funded Tri-Services program to develop prebond surface preparations and hybrid primers utilizing sol-gel technology on aluminum, titanium, and steel substrates. The report summarizes optimization work to improve the reproducibility and robustness of the sol-gel surface preparations and hybrid primers. The project focuses on the development and optimization of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure and 350°F-cure epoxy adhesives. Several improvements to the Boegel-EPII materials and processes were identified in this work. For example, it was determined that addition of a surfactant can improve the appearance and uniformity of the sol-gel coatings, but is not critical to achieving good performance on these alloys.

Studies indicate that careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Under carefully controlled laboratory conditions, it is possible to yield good performance for many of the abrasive media, but when subjected to conditions that mimic a repair scenario, only a few of the abrasive media gave reproducible performance. Surface contamination on the metal was a result of smeared adhesive, overheating of the abrasive pad or tool, or unacceptable cleaning of the surface. Performance using downselected abrasive media and tools was verified using hot/wet testing, such as the Boeing wedge test and double cantilever beam testing. Procedures were documented calling out all of the preferred materials and processes.

The development of a new hybrid primer system, combining aspects of the surface treatment and adhesive bond primer, was also a focus of this effort. Progress was made towards identifying an effective hybrid inorganic/organic polymer chemistry and developing the system to result in a candidate room-temperature bond primer that can be used in conjunction with low-temperature-curing two-part paste adhesive systems.

The results of these studies, including bond performance and durability as well as surface characterization, are summarized in this report.

2 Introduction

2.1 Background

The Strategic Environmental Research and Development Program (SERDP) has funded a Tri-Service team to develop prebond surface preparations and hybrid primers utilizing sol-gel technology on aluminum, titanium, and steel substrates. This project focuses on the development and optimization of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure and 350°F-cure epoxy adhesives. The goals of this program are to design processes that 1) use environmentally friendly materials, 2) increase durability, 3) improve process robustness, 4) decrease repair time, 5) use simple equipment and procedures, and 6) increase affordability. Depot sites, including NADEP-North Island, NADEP-Cherry Point, NADEP-Jacksonville, Warner Robins ALC, and Corpus Christi Army Depot are involved in the requirements generation and testing cycle to ensure end-user needs are being met and technology transition issues are assessed.

Previous work[1] by the SERDP Team developing these sol-gel surface treatments has shown significant progress toward user-friendly sol-gel surface preparation methods for repair and original equipment manufacturing (OEM) bonding. Processes for repair were designated using grit-blasting as the preferred method of deoxidation on the surface prior to application of the sol-gel. Continued work on non grit-blast pretreatment methods revealed differences in performance of the bonded specimens during hot/wet exposure of the sol-gel prepared specimens.

This report summarizes optimization work on the non grit-blast pretreatment methods in conjunction with the use of the sol-gel surface preparations and hybrid primers using the Boegel-EPII materials and processes on metal alloy substrates.

2.1.1 Surface Treatments

Aircraft repair manuals or technical orders typically require the use of surface preparations such as tankline phosphoric acid anodize (PAA), manual PAA (PACS or PANTA)[2], hydrofluoric acid (HF)/Alodine®, or acid paste etches for the repair of aluminum alloy structure. These surface preparations rely on hazardous acids and/or time-consuming and complex processing steps. Lack of process robustness results in some bonding repair practices that do not consistently yield the expected bond performance. The phosphoric acid in PAA and sulfuric acid used in common paste acid etches (Pasa-Jell), are difficult to contain and rinse off when conducting on-aircraft repairs of complex shapes and assemblies. The HF in HF/Alodine® is a health hazard.

A grit-blast/silane surface preparation has been employed in many military repairs. It provides an alternative to the use of acids, but requires a grit-blasting step, elevated-temperature drying, and several hours to perform[3]. The grit-blast method is also less desirable for repair applications due to concerns regarding containment of the material in a field or depot setting. The sol-gel process is similar to the silane surface preparations currently used, but it has a number of advantages. It is quicker, eliminates the elevated-temperature drying step, and can eliminate the grit-blasting step in many applications.

The sol-gel process tested here involves the use of the Boeing-developed Boegel-EPII formulation, which is currently commercially available as AC-130 from Advanced Chemistry and Technology (AC Tech, Garden Grove, CA). This aqueous-based sol-gel solution can be brushed or sprayed on the surface to be treated and does not require rinsing.

The sol-gel surface preparation process works by producing a gradient interphase coating. One side is molecularly bonded to the oxide structure on the metal and the other side is molecularly crosslinked with the adhesive primer (Figure 2.1-1). The type of bonding at the metal interface determines the long-term durability of the system. For high-performance durable bonding the metal alloy surface must be scrupulously clean and have an active metal oxide surface chemistry. Contamination on the surface can reduce the number of surface reactive sites and subsequently reduce the surface density of bonds with the sol-gel coating. This will reduce the ultimate durability of the system.

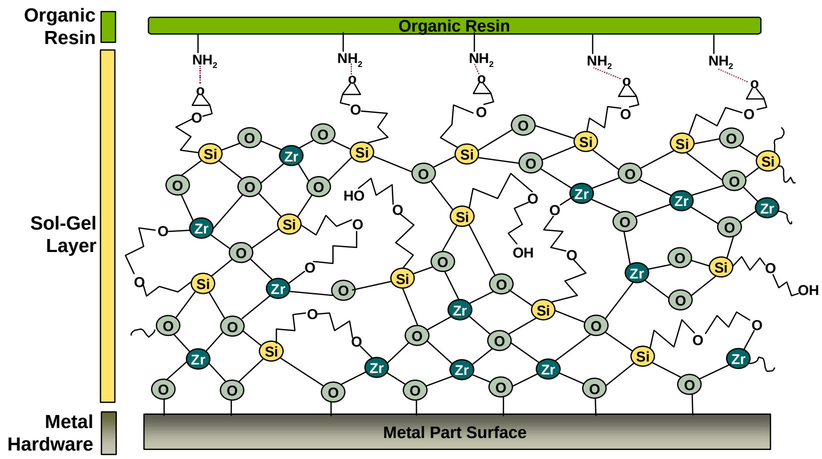


Figure 2.1-1 Notional Schematic of Sol-Gel Adhesion-Promoting Coating on a Metal Part

2.1.2 <u>Hybrid Primers</u>

A second task in this program was development of a hybrid adhesive primer coating. The focus of the hybrid effort was to develop a room-temperature-curing nonchromated waterborne primer for use with paste adhesive systems. Currently, there is no suitable bond primer system that can be cured at room temperature yet still produce bonded joints with acceptable strength and durability properties using paste adhesive systems.

To produce these new hybrid polymer systems, an approach based on hybrid copolymer or polymer blend technologies was employed. This approach is defined by using the traditional methodologies of organic polymer chemists, but using new polymer feedstocks. A polymer blend in traditional organic polymer terminology is where a portion of one type of polymer is mixed with a portion of another type of polymer. These general approaches are depicted in Figure 2.1-2.

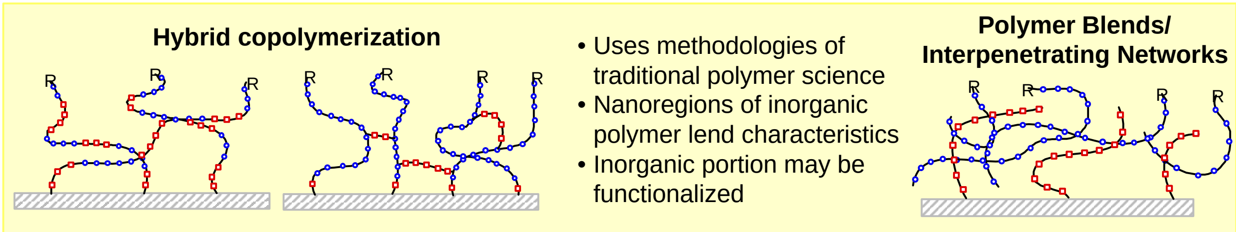


Figure 2.1-2 Hybrid Adhesive Primer Development Approaches

3 Experimental Procedures

3.1 Materials

3.1.1 General

This program examines the use of the sol-gel surface treatments on metal alloy systems. In this report, testing was conducted on 2024-T3 bare alloy, unless otherwise noted. Testing was conducted in a laboratory setting under ambient temperature and humidity conditions. No specific controls of the conditions were accounted for during this testing.

Unless otherwise noted, the process outlined in Table 3.1-1 was used to bond aluminum test specimens.

Table 3.1-1 Process Method Used to Prepare Sol-Gel Test Specimens

Step #	Process
1	Solvent wipe with Methyl Ethyl Ketone (MEK) followed by acetone until cheesecloth is clean.
2	Abrade using a random orbital sander or die grinder.
3	Blow off loose particles with clean dry air.
4	Spray surfaces with Boegel-EPII (AC-130) for 2-3 minutes, keeping surfaces wet. Apply sol-gel within 30 minutes of abrasion.
5	Dry at ambient temperature for one hour.
6	Spray apply adhesive bond primer, Cytec BR 6747-1.
7	Apply adhesive, AF163-2M.
8	Cure at 250°F in autoclave at 45 psig (60 to 75 minutes).

3.1.2 Manual Deoxidation Materials and Equipment

The sanding process was carried out using a random orbital sander or a die grinder, both fitted with a filtered rear exhaust, Table 3.1-2.

Table 3.1-2 Surface Preparation Tool Details for Sandpaper Variation Study

Surface Prep Tools	Manufacturer	Abrasive diameter	Speed
Random Orbital Sander	Dewalt	5 inch	10,500 orbits/minute
Die Grinder	Myton	5 inch with 3-inch backing pad	20,000 rpm

The abrasion process involved sanding with the candidate abrasive paper or pad for one to two minutes over approximately 6 in x 6 in sections. The sander was guided from side to side across the entire 6 in x 6 in area and abraded in a perpendicular direction to achieve one cross-coat. The sandpaper was changed when it became worn, as evidenced by tears, seizing of the tool, and clogging. At a minimum, one fresh piece of sandpaper for each 6 in x 6 in area was used. The

sanding speed was adjusted in particular experiments and tended to range from a one to two minute period over a 6 in x 6 in area. Figure 3.1-1 summarizes the abrasion procedure.

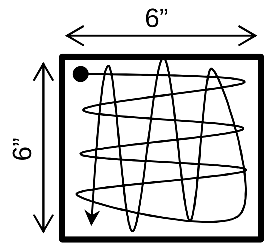
Area/Sanding Pattern	
Sandpaper Changeout	1 piece/36 in^2
Time Sandpaper Used	1-2 min/36 in^2

Figure 3.1-1 Abrasion Process Summary

After completion of the sanding procedure, loose grit was removed from the surface of the specimen using clean, dry compressed air or nitrogen. No wiping of the surface, either dry or with solvent, was carried out in any of the testing. Unless otherwise noted, the specimens were coated with the sol-gel solution within 30 minutes of the abrasion process.

3.1.3   Sol-Gel Chemistries

Versions of the waterborne silicon-zirconium sol-gel system, Boegel-EPII, were tested throughout this program. This formulation is commercially sold as AC-130 by AC Tech. Changes to the formulation and application chemistry were carried out as noted in the sections of this document.

The sol-gel solution was typically spray applied on the surface of the specimens, which were positioned vertically on a spray rack. The solution was reapplied several times, keeping the surface wet for a period of two minutes. Sol-gel application is generally carried out using spray equipment such as a high volume, low pressure (HVLP) spray gun, a manual pump spray apparatus, or a clean, natural bristle brush. Then the specimens were allowed to drain and dry for a minimum of 60 minutes before an adhesive primer was applied. In all cases, adhesive primer was applied within 24 hours of sol-gel application.

3.1.4 Primers and Adhesives

Cytec Fiberite BR 6747-1 adhesive bond primer was chosen as the baseline bond primer for testing in this program. The primer was spray-applied to the surface using an HVLP gun to a dry film thickness of 0.15 – 0.40 mils. The primer was cured at 250°F for 60-90 minutes per the Boeing BMS5-89 specification.

For 250°F-cure BMS5-101 film adhesive testing, specimens were bonded with 0.06 psf AF 163-2M film adhesive from 3M Company, unless otherwise noted. The adhesive was cured for 60-90 minutes at 250°F and 35-40 psi in an autoclave, unless otherwise noted.

3.1.5 Hybrids

The baseline hybrid formulation used in this work was developed previously[1] and is designated RS-HY. RS-HY, a bidentate silane triol/BPA epoxy blend, was formulated from hydrolyzed and partially prereacted (3-glycidoxypropyl)trimethoxysilane and EpiCure™ 8290-Y-60 (from Resolution Performance Products) blended with waterborne EpiRez™ 5522-WY-55 epoxy and EpiCure™ 8290-Y-60 curing agent.

3.2 Testing

3.2.1 Performance and Durability Testing

The primary screening test used in this program, intended to assess the long-term environmental durability of the bonded joints is the wedge test (ASTM D 3762).[4] Treated adherends, sized 6 in x 6 in, are bonded together, and the panels are machined into 1-in wide specimens. The thickness of the panels used in the screening studies was a function of the alloy used. Typically for aluminum alloys, the nominal sheetstock thickness used was 0.125 in. A wedge is inserted into one end of the specimen bondline and the resultant crack generated within the adhesive is measured. The sample is placed in a hot/wet environment and the crack length is measured periodically. For screening purposes, bonds exhibiting at least 95% cohesive failure within the adhesive with minimal crack growth after 28 days are considered acceptable.

The environmental conditions utilized are 140°F and >98% RH. The crack growths and failure modes of the specimens were used to calculate the significance of each factor tested. Most wedge test specimens with optimum processing conditions exhibited crack growths of <0.25 inches with cohesive failure modes (within the adhesive layer). Small “nicks” of adhesive failure (at the metal interface) were sometimes detected at the edges of these specimens. It was estimated that the area of these small nicks was roughly 5% or less of the specimen test area. Failure modes for all developmental specimens are reported in conjunction with the wedge crack extension data.

Additional screening utilized tensile lap shear per ASTM D 1002 [5] as well as climbing drum peel testing per Boeing specification BSS 7206, floating roller peel testing to both BSS 7206 and ASTM D 3167[6] and double cantilever beam (DCB) testing per Boeing specification BSS 7208.

3.2.2 Surface Analysis

An ESCA (Electron Spectroscopy for Chemical Analysis) survey-scan was performed on sample specimens treated with candidate abrasive media to determine the ability of the media to remove the outer oxide layer and the relative cleanliness of the abraded surface. ESCA was also performed on the abrasive media itself before and after use. The ESCA system is a Surface Science Instruments Series 300 x-ray photoelectron spectrometer equipped with a monochromatic Al K-alpha x-ray source, hemispherical analyzer, and multichannel detector. The system is calibrated using the Au 4f7/2 peak at 84.00eV binding energy. The data were taken using an 800 micron diameter spot size x-ray beam. The ESCA analysis area in each case is 1mm in diameter and ~30 angstroms deep.

The surface roughness of each of the abraded aluminum samples was measured using a Wyko NT2000 Optical Profiler. This equipment uses vertical scanning interferometry to measure the profile of surfaces. It has a 10 x 0.5 objective and reports roughness values in μin.

3.2.3 Impact / Adhesion Testing

Hybrid primer-coated specimens were also evaluated for adhesion using impact adhesion and GE impact tests in accordance with Boeing specification BMS10-72 and ASTM D 522.[7] Both sides of impact adhesion panels are subjected to an impact of 80 inch pounds using a Gardner 160 inch pound capacity impact testing machine with a 0.625 inch diameter hemispherical indenter. Adhesion is then determined by tape testing the coated side of the panel at the point of impact. The requirement for this test per BMS10-72 is no cracking or loss of adhesion at 80 inch pounds forward or reverse impact. GE impact panels are tested by impacting the uncoated side of the specimen simultaneously with four convex spherical segments, each of different radii and extension, in a GE Universal Impact-Flexibility Tester, Model 172 (or equivalent). The sample is then inspected using 10 power magnification to examine surface cracking; the percent elongation corresponding to the largest spherical impression at which no cracking occurs is reported. The requirement per BMS10-72 is for no cracking or loss of adhesion at 60 percent elongation.

4 Aluminum Results

4.1 Chemical Optimization

4.1.1 Summary

During previous work, the addition of surfactants to the sol-gel solution was shown to be beneficial for improved wetting of the metal substrate. Therefore, a small screening study was performed during this work to further characterize the effects of surfactant addition. Two surfactants tested gave visually improved wetting. However, because there is no surfactant in the currently available AC-130 kit specifications, implementation of the surfactant-containing solutions will not be pursued.

4.1.2 Screening Study

Two new surfactants, Rhodia Antarox BL-240 (an ethoxylated/propoxylated alcohol) and Tomadol 91-8 (an ethoxylated alcohol) were identified as possible replacements to the discontinued 3M FC170C to improve sol-gel coating uniformity on the surface. The 3M FC170C was a fluoroaliphatic oxyethylene. All of the candidate surfactants come from similar chemical families. In screening testing, both the Antarox BL-240 and the Tomadol 91-8 vastly improved coating uniformity over metal surfaces, virtually eliminated the uneven wetting pattern on the surface and drying patterns in from the edges of test specimens.

While both surfactants appear to be viable choices for incorporation into the sol-gel formulation, the Antarox was chosen as the one that gave slightly better appearance properties. Doping of the sol-gel solution at levels ranging from 0.01% to 0.1% by weight of the total solution was evaluated to determine its effect on system performance.

To test the wetting capabilities of the highest loading level and determine whether addition of the surfactant would cause any detrimental adhesion problems, a sol-gel solution doped with 0.1% Antarox was formulated in the lab. Wedge and peel test specimens were precleaned in Brulin 815 alkaline cleaner for this study. Three different sandpapers were tested. Specimen C80-6 used a 3M 210 #220 alumina 5-in wide sandpaper disc. Specimen C80-9 used a Merit #180 ALO 5-in diameter Shur Stik alumina grit resin bond sandpaper. The C80-14 used the Merit Zirc-Plus (green) #120 5-in diameter Type II Power-Lock with a 3-in backing pad on a die grinder.

All specimens were sanded with each surface being manually sanded for an approximately 60 second period with one piece of sandpaper per metal specimen going over the surface in a cross-hatch pattern to ensure coverage of all areas. The specimens were then sprayed with the surfactant-doped sol-gel solution within 30 minutes of sanding. The drying pattern for these specimens was very different than in previous testing. After the sol-gel had dried, it was virtually impossible to tell that there was a sol-gel coating on the surface at all. This is good for uniformity, but undesirable for inspection purposes.

4.2 Abrasive Media Screening Studies

4.2.1 Summary

As part of the technology transition efforts, training of individuals who are interested in implementing the sol-gel process was conducted on a regular basis. For the purpose of this program, the training sessions were coupled with durability testing to gather a database on the reproducibility of the system and robustness of the processes.

This section also details efforts to test various abrasion-based pretreatment processes to determine which show the robustness necessary to be carried to secondary durability testing.

4.2.2 Process Demonstration Trials

Initial Demo Comparison: A demo was conducted with personnel from Abaris Training, a firm that specializes in training people on composite and metallic bonded repair for aerospace structures. In this study, panels were mechanically deoxidized using two candidate sandpapers. Two sets of aluminum 2024-T3 were precleaned in the Brulin 815 alkaline cleaner for this study. A 500 mL Boeing sol-gel kit was mixed and utilized for this demonstration. Specimen HP120 was sanded using 5-in diameter Merit Abrasives Part #65191 Power-Lock #120 zirconia grit sandpaper discs mounted on a die grinder. This paper was recommended by The Nordam Group from their screening tests of various sandpapers and reproducibility of testing.

Specimen HP220 was sanded using standard 3M #220 326U alumina sandpaper discs. The details of the chemistry of the glue on the disc and abrasive were clarified with the 3M Company. Informal telephone conversations indicate that the adhesive used to bond the abrasive media to the sandpaper contained an adhesive designed for the treatment of wood-based surfaces that might cause potential contamination of the metal surface.

The samples were primed using Cytec BR 6747-1 waterborne primer and cured at 250°F for 60 minutes, then bonded with 3M AF 163-2M film adhesive. Final wedge test results and failure modes are shown in Figure 4.2-1. After 30 days of exposure to 140°F and >98% relative humidity, wedge test coupons were broken open for comparison of failure modes.

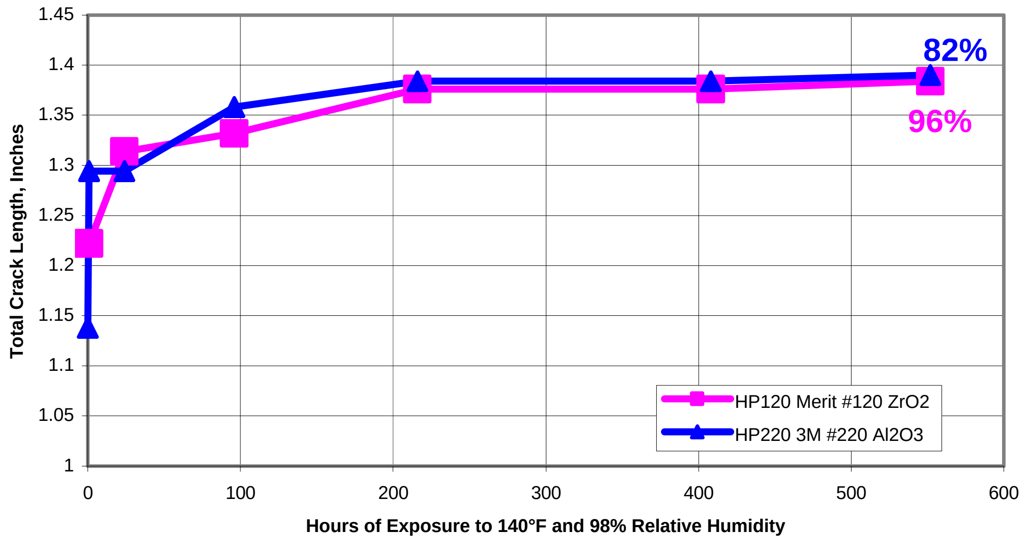


Figure 4.2-1 Wedge Test Data for Sandpaper Comparison of a Merit Zirconia Sandpaper with 3M Alumina Sandpaper.

From these studies, it was clear there was a difference in the cohesive failure modes between specimens deoxidized with the different sandpapers. The #220 grit alumina 3M 326U paper gave a cohesive failure mode of 82% versus 96% from the Merit Zirc+ #120 grit alumina/ zirconia paper. This is potentially indicative of some residue left on the surface from the use of this 3M sandpaper.

4.2.3 3M-Prepared Specimens

Meetings were held at the 3M Technology Center in St. Paul, MN to discuss the results that were obtained using the 3M off-the-shelf sandpapers versus the Merit Abrasives sandpapers. Results had shown that the selected Merit sandpapers performed better, yielding more cohesive failure than the 3M papers. The technical specialists at 3M recommended several new sandpapers containing adhesives and grit media more appropriate for metal treatment prior to sol-gel. Specimens using these abrasive materials were prepared on-site at the 3M abrasives facility.

Five sets of 2024-T3 aluminum alloy were precleaned with methyl ethyl ketone. The specimens were abraded with tools and abrasive media recommended by 3M, according to the data in Table 4.2-1. A sol-gel kit assembled at Boeing had been sent to the site for this testing. The sol-gel kit was mixed on site in preparation of the specimen fabrication. The freshly abraded specimens were coated with the sol-gel solution using a brush of unknown origin while horizontally placed in a small tray. The panels were then propped up to drain and dry for a minimum 30 minute period. It was noted that this was not the best set-up for the experiment. There were many variables that were uncontrolled that may have had an effect on the end results of the experiment. For example, the solvents, brushes, wipe cloths, and laboratory conditions were not well controlled. There was a significant amount of grit and particulates remaining on the surface in

the sol-gelled and dried panels. However, the demonstration continued in order to understand technique issues regarding application of the 3M-recommended abrasives and tools.

Table 4.2-1 Abrasive Tools and Media Used in 3M Demonstration Panels

Specimen #	Tool	Abrasion Media
3M-1 Sample #1-2	Random Orbiter Sander, ARO Model RS25a-CSV, 1200 RPM; 3M 5-in Backup Pad (05545), Stick-It	268L 60 Micron, 5-in disc, Type D
3M-2 Sample #3-4	Random Orbiter Sander, ARO Model RS25a-CSV, 1200 RPM; 3M 5-in Backup Pad (05545), Stick-It	268L 80 Micron, 5-in disc, Type D
3M-3 Sample #5-6	Random Orbiter Sander, ARO Model RS25a-CSV, 1200 RPM; 3M 5-in Backup Pad (05545), Stick-It	210U P180
3M-4 Sample #7-8	Right Angle Die Grinder, High Speed, 15,000 RPM; 3M 3-in Roloc Pad	SE A Fine
3M-5 Sample #9-10	Straight Shaft Grinder, 18,000 RPM Dynabrade 51025; 3M 990 Mandrel	Bristle disc 220x, stacked 9 discs

Note: All samples made with Boegel EPII, 3M EC 3963 primer, 3M AF 163-2M Adhesive

The panels were dried for a minimum of 30 minutes and wrapped in laboratory paper towels, stored overnight, then transported to the Adhesives Building. The next morning, they were primed with the latest developmental version of the 3M EC 3963 waterborne primer. It was noted that this primer is still in development and some adjustment of the formulation is still taking place to optimize wedge test and peel behavior. The results of these tests do not necessarily indicate that the processing methods described herein will not work. Additionally, this was the first test of this new primer formulation and it was unknown how it would perform in conjunction with sol-gel. Similar specimens were fabricated in the Boeing Laboratories using similar tools to validate the testing being conducted during these trials. The primer was applied on the specimens by 3M personnel to a dry film thickness range of 0.21 to 0.29 mils within the ten panel sample set. The panels were cured in an oven at 250°F for 60 minutes. The panels were then wrapped and shipped to Boeing. At Boeing, the specimens were bonded using 3M AF 163-2M adhesive.

The wedge test results are shown in Figure 4.2-2. One finger from each of the specimen sets was removed at 24 hours for analysis of the failure mode. Upon breaking the specimens open, the failure appeared by visual analysis to be at the metal interface; it was not determined whether the failure was at the metal-to-sol-gel or sol-gel-to-primer interface. As mentioned before, this test was not necessarily indicative of the results that can be achieved using these abrasive tools.

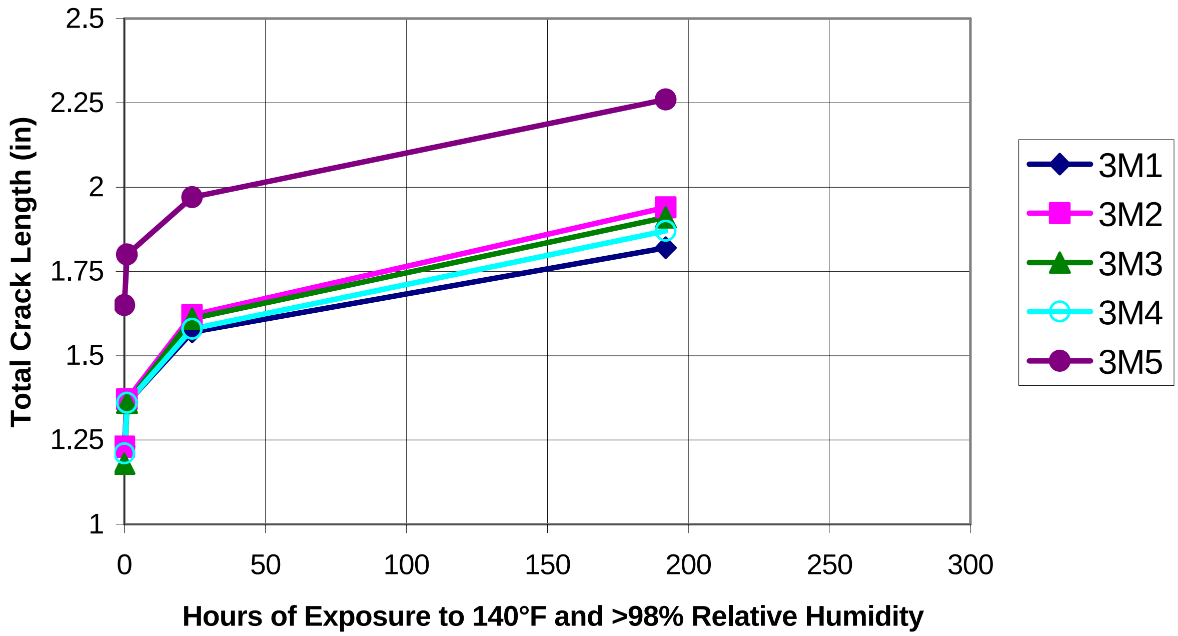


Figure 4.2-2 Wedge Test Results from 3M Demonstration Panels Using Various Abrasion Media and Tools as Described in Table 4.2-1

4.2.4 3M Study Repeated at Boeing

As a follow-up to the samples prepared at 3M, the five variants of abrasive media that were examined in Minnesota were tested in the Boeing Laboratories. From previous studies, it was found that all of the abrasive media tested at the 3M facility performed relatively poorly when used in conjunction with the developmental 3M primer and applied on-site at that location. There were many uncontrolled parameters in that study, so the tests were completed at Boeing using a different primer, Cytec BR 6747-1. Details of the abrasive media and techniques employed are described in Table 4.2-2.

Specimens in this study were solvent wiped and then tankline-cleaned in Brulin 815GD. Boegel-EPII was prepared and applied to the manually abraded surface within 30 minutes of the abrasion process in each case. Peel specimens and wedge specimens were layed up for every test configuration. For specimen #5, there were not enough 220X bristle discs to make the duplicate wedge test panels, so 120X bristle discs were used instead, as noted in Table 4.2-2. Figure 4.2-3 shows the wedge crack extension performance of these specimens. All specimens exhibited approximately 98% cohesive failure after 4 weeks, except for the bristle disc specimens, which had 0% cohesive failure.

Table 4.2-2 Abrasive Media Variations for 3M Repeat Study Conducted in Boeing Laboratories

Treatment Number	Abrasive	Tool	Details
1.	#268L 60 micron, 5-in disc	Random Orbital Sander, DeWalt	Use 1 disc for each 6 in x 6 in area. Abrade each 6 in x 6 in area for 2 minutes.
2.	#268L 80 micron, 5-in disc	Random Orbital Sander, DeWalt	Use 1 disc for each 6 in x 6 in area. Abrade each 6 in x 6 in area for 2 minutes.
3.	#210U P180A, 5-in disc	Random Orbital Sander, DeWalt	Use 1 disc for each 6 in x 6 in area. Abrade each 6 in x 6 in area for 2 minutes.
4.	Roloc pad SE A fine, 3-in disc	Die Grinder, Myton	Use 1 disc for each 6 in x 6 in area. Abrade 2 cross-coats (~ 1 minute).
5.Peel	Bristle disc, 220X, stack of 10	Die Grinder, Myton	Bristle discs not changed. Abrade 1 cross-coat.
5. Wedge	Bristle disc, 120X, stack of 10	Die Grinder, Myton	Bristle discs not changed. Abrade 1 cross-coat.

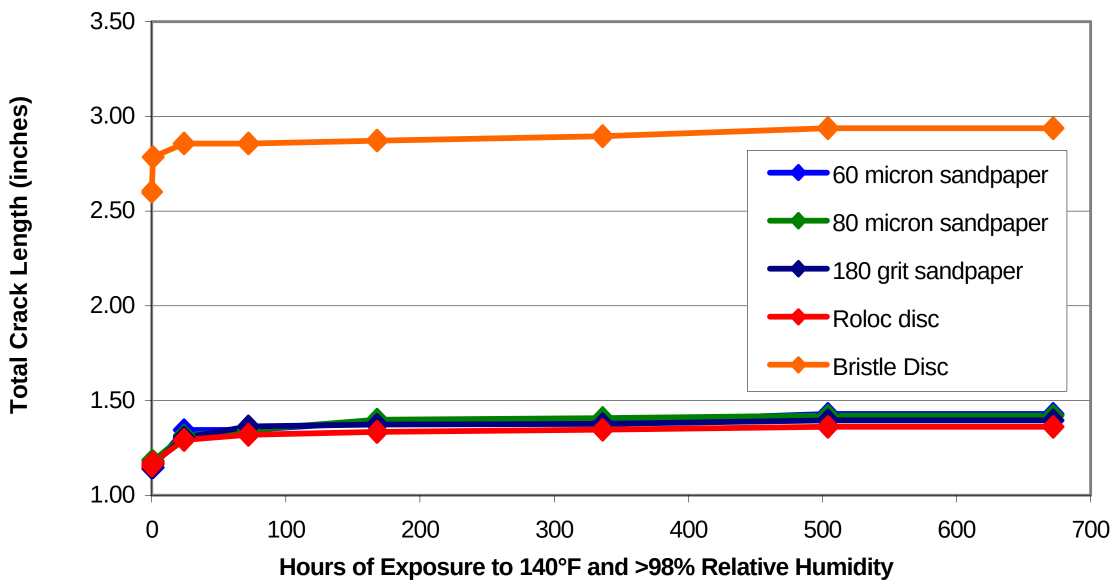


Figure 4.2-3 Wedge Test Comparison of 3M Abrasive Media with Sol-Gel Processing

Peel specimens were also prepared to understand the peel behavior associated with the different abrasive media and techniques. Both peel strengths and failure modes are shown in Figure 4.2-4.

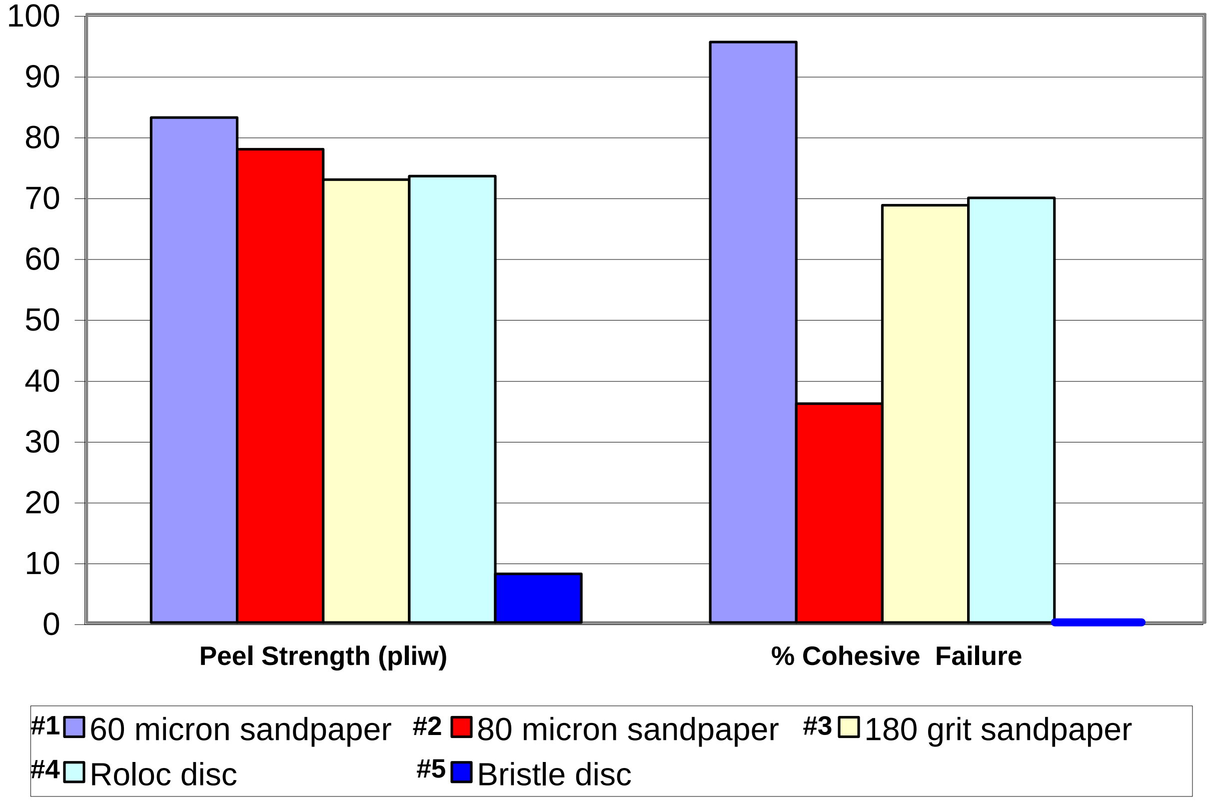


Figure 4.2-4 Climbing Drum Peel Test Comparison of 3M Abrasive Media with Sol-Gel Processing

The peel strengths for the different abrasive media were all similar with the exception of the bristle disc, which yielded substantial degradation in peel properties. The cohesive failure modes for the peel specimens varied a bit, with the 60 micron 3M 268L cubitron paper showing the best performance. It was unclear from this study what caused the differences in peel failure modes. The wedge test specimens all gave similar results, with the exception of the bristle disc.

4.2.5 3M 216, Merit SK-62, and Merit Zirc-Plus

Additional screening studies were conducted to determine process reproducibility with some of the abrasive materials that had shown decent performance in the preliminary screening studies. Two alumina-grit sandpapers from 3M were selected as was one alumina grit sandpaper from Merit Abrasives. These papers were compared against a Merit #120 zirconia paper “control” which had shown previous success. Table 4.2-3 describes the various sanding media and sample preparations.

Table 4.2-3 Sanding Media Variations for Surface Preparation Study Using Various Abrasive Media.

Specimen No.	Surface Prep Tool	Surface Prep Abrasive
C80-4	Random Orbital Sander	3M 216U-P180
C80-6	Random Orbital Sander	3M 216U-P220
C80-9	Random Orbital Sander	Merit SK-62-P180
C80-14	Die Grinder	Merit 120 Zr+

Note: All samples made with BoeGel EPII + 0.10% surfactant* and Cytec BR 6747-1 primer.
* surfactant = Rhodia Antarox BL-240

Two sets of 2024-T3 bare wedge test panels were prepared for each type of abrasive paper. Specimens were precleaned using a Brulin 815GD aqueous degrease and an alkaline clean with Isoprep 44 to obtain a uniformly clean surface on all panels. The surfaces were abraded using one piece of sandpaper per 6 in x 6 in area for one minute, alternating the direction of the tool travel by 90 degrees after each complete pass. The panels were then blown off with nitrogen. The sol-gel was applied by spraying with an HVLP gun within 30 minutes of abrasion. Specimens were primed with Cytec BR6747-1 adhesive bond primer and cured for 75 minutes at 250°F. Wedge test specimens were bonded with AF 163-2M adhesive and cut into 1-in wide specimens. Exposure of specimens at 140°F and >98% relative humidity for 30 days gave the results shown in Figure 4.2-5. Failure mode analysis after 24 hours of exposure is shown in Table 4.2-4.

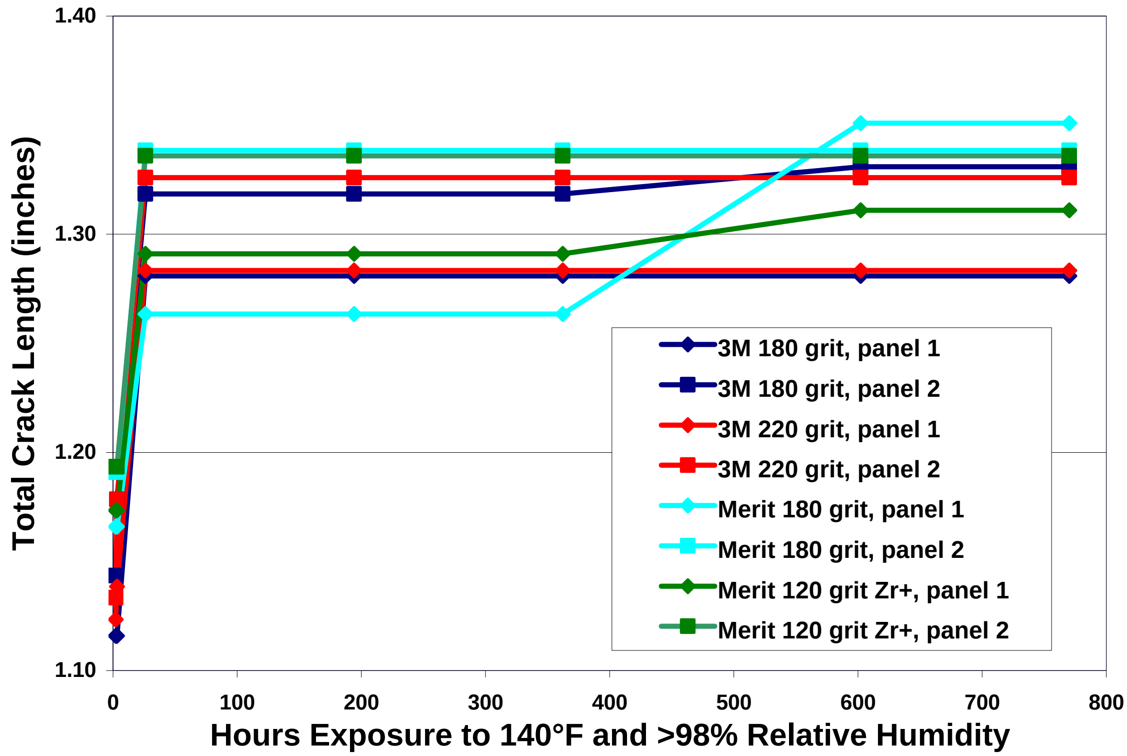


Figure 4.2-5 Wedge Test Comparison of New Sandpapers with Sol-Gel Processing

Table 4.2-4 Failure Modes for Sandpaper Deoxidized Sol-Gel Coated Specimens After 24 Hrs of Exposure to 140°F and >98% RH in the Wedge Test

Specimen #	Type of Sandpaper Used	Failure Mode (% Coh)
C80-4-1	3M 216U-P180 (alumina)	95%
C80-4-2	3M 216U-P180 (alumina)	98%
C80-6-1	3M 216U-P220 (alumina)	90%
C80-6-2	3M 216U-P220 (alumina)	99%
C80-9-1	Merit SK-62-P180 (alumina)	98%
C80-9-2	Merit SK-62-P180 (alumina)	98%
C80-14-1	Merit #120 Zirc-Plus (zirconia)	98%
C80-14-2	Merit #120 Zirc-Plus (zirconia)	99%

These data indicate that the manual deoxidation process used in this study with the alumina abrasive papers chosen did not appear to cause contamination of the surface resulting in a degradation of the sol-gel coating performance. However, excessive pressures or rpm levels on the tools, or overuse of the abrasive materials, may cause overheating of the adhesively-bound abrasive material pads, resulting in smearing of organic material on the metal surface. These potential differences are not easily uncovered in a controlled laboratory testing. Systematic testing of the sandpapers was attempted (see next section) to help elucidate conditions which may result in failure.

4.3 Systematic Abrasive Media Study

4.3.1 Summary

Several early studies highlighted the variability in performance when using different abrasive media and tools to deoxidize the aluminum surface prior to sol-gel application. To that regard, a systematic study was conducted to evaluate the different surface chemistries of the different abrasive products, comparing them directly to the performance that is achieved in a controlled experiment. Seven different abrasive media were used; peel, wedge test, and DCB data were measured for all seven candidates. In addition, ESCA, scanning electron micrography, and profilometry were performed on Al substrates treated with the abrasive media as well as control specimens. ESCA and scanning electron micrography were also run on abrasive media samples.

4.3.2 Test Matrix

To determine effects on surface contamination and morphology, Al2024-T3 panels were prepped with the different sandpapers and abrasive media shown in Table 4.3-1.

Table 4.3-1 Abrasive Media Matrix

No.	Sandpaper/Abrasive Media	Method
1	3M 210U-P180	Random Orbital Sander
2	Merit SK-62-P180	Random Orbital Sander
3	Merit 120 Zirc-Plus	Die Grinder
4	3M 268L 80 Micron, 5-in disc, Type D	Random Orbital Sander
5	3M 326U #220 alumina	Random Orbital Sander
6	Standard Abrasives A/O Xtra, #120 grit, Type I Lockit	Die Grinder
7	Scotch-Brite medium roloc disc (maroon)	Die Grinder
C1	Solvent Wipe	N/A
C2	Chemical Deoxidation	N/A

Two specimens were prepared, sized 6 in x 6 in x 0.125 in, with each surface preparation. These samples were used for ESCA, SEM analysis, and profilometry. In parallel, specimens were fabricated using the same abrasives described above in order to conduct performance and durability testing (wedge test, DCB, climbing drum peel) to determine bond strength differences in Al2024-T3 specimens. Boegel-EPII solution, precured Cytec BR 6747-1, and 3M AF 163-2OST were used to fabricate the performance trial specimens.

4.3.3 Performance Test Results

Peel

The peel test results for the matrix are shown in Figure 4.3-1. All specimens showed 100% cohesive failure at room temperature testing.

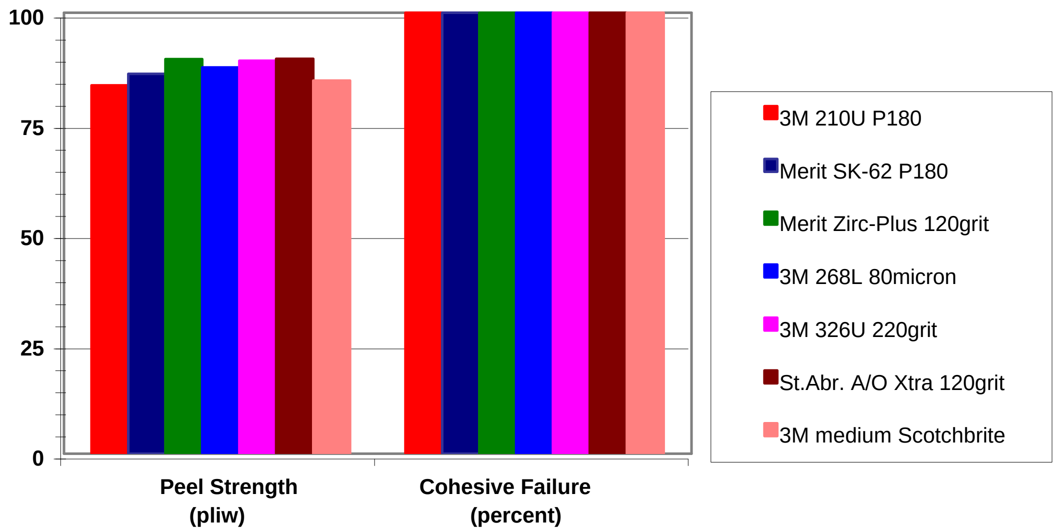


Figure 4.3-1 Climbing Drum Peel Test for Different Sandpaper Abrasives Used Prior to Sol-Gel Treatment

All of the different abrasive pretreatments resulted in climbing drum peel values over 80 pound-inches per inch of specimen width (pliw). The failure modes were all 100% cohesive, regardless of pretreatment. Once again, it was observed that under controlled laboratory conditions, with a trained technician, it is possible to make all of the abrasive materials yield acceptable performance.

Wedge Test

Wedge crack extension data are shown in Figure 4.3-2. Failure mode data are shown in Table 4.3-2; two columns of failure modes are listed. The first column is the average failure mode of 4 of the 5 “fingers” (one finger of each specimen having been pulled out of the exposure chamber at 984 hours for inspection); these values are considerably lower than expected. The second column lists the average failure mode of 2 specimens from the center of the specimen, position number 2, 3, or 4. These values are consistent with previous data, indicating an edge effect not previously seen in samples processed in this laboratory, but noted in samples processed elsewhere. (Note: A 60 micron 3M 268L paper was substituted for the #4 80 micron 3M 268L paper in this test after supplies of the 80 micron paper were exhausted.)

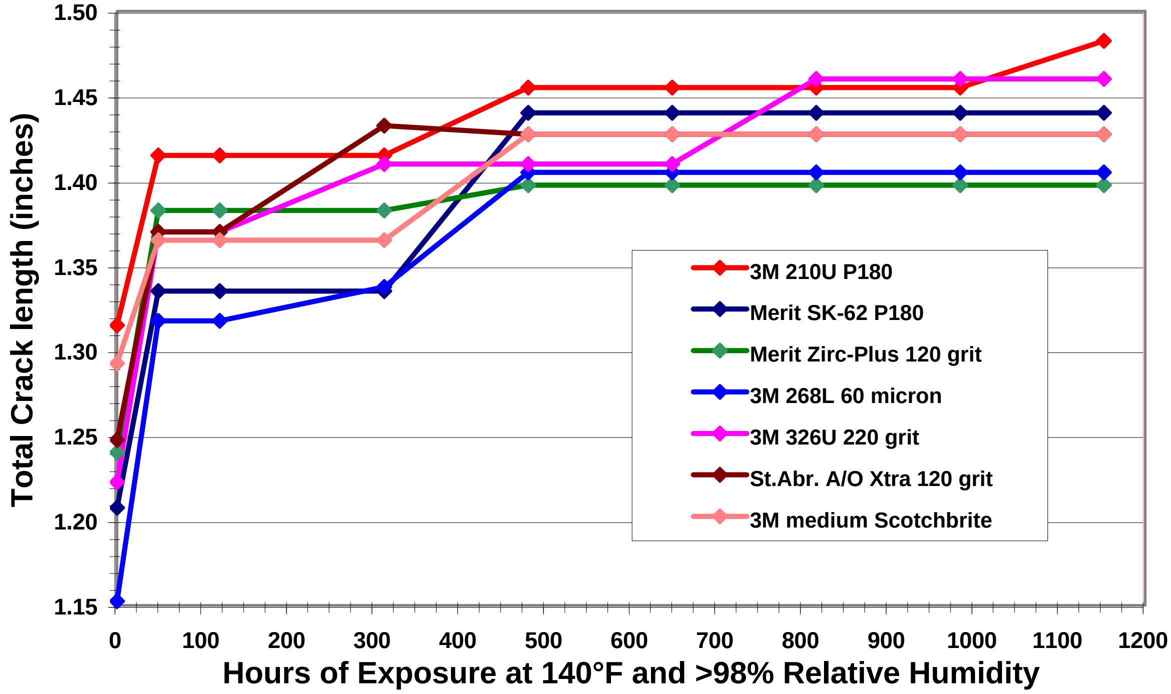


Figure 4.3-2 Wedge Test Results for Abrasive Media Variations

Table 4.3-2 Failure Modes for Wedge Tests

No.	Sandpaper/Abrasive Media	Percent Cohesive Failure*	Percent Cohesive Failure**
1	3M 210U-P180	73	90
2	Merit SK-62-P180	73	85
3	Merit 120 Zirc-Plus	80	93
4	3M 268L 80 Micron, 5-in disc, Type D	68	85
5	3M 326U #220 alumina	56	67
6	Standard Abrasives A/O Xtra, #120 grit, Type I Lockit	75	93
7	Scotch-Brite medium roloc disc (maroon)	71	93

***Average of 4 specimens from sample positions 1-5**

****Average of 2 specimens from sample positions 2-4**

Double Cantilever Beam Results

DCB specimens were also fabricated in parallel with the wedge test specimens as a more severe measure of the interfacial environment. Environment Crack Extension Force (G_{Iscc}) has been calculated for 15 weeks of exposure; results are shown in Figure 4.2-3 and Table 4.2-3.

The minimum requirement as listed in the 250°F-cure epoxy film adhesive specification, BMS5-101, is 3.5 in-lbs/in^2 after 5 weeks exposure. All of the abrasive media and tools tested were above that minimum value. The requirement for 15-week exposure (per BMS5-101) is for the G_{1scc} to be 70% of what it was at 5 weeks. Specimens 3, 5, and 6 passed this requirement, which is based on samples prepared with PAA. All of the specimens exhibited a marked decrease in G_{1scc} after 11 weeks, possibly indicating a change in conditions in the exposure chamber. After continuing the exposure to 15 weeks, the specimens were all broken open for examination and measurement of the failure modes; average cohesive failure is shown in Table 4.3-3 and photos of the specimens are included in the Appendix.

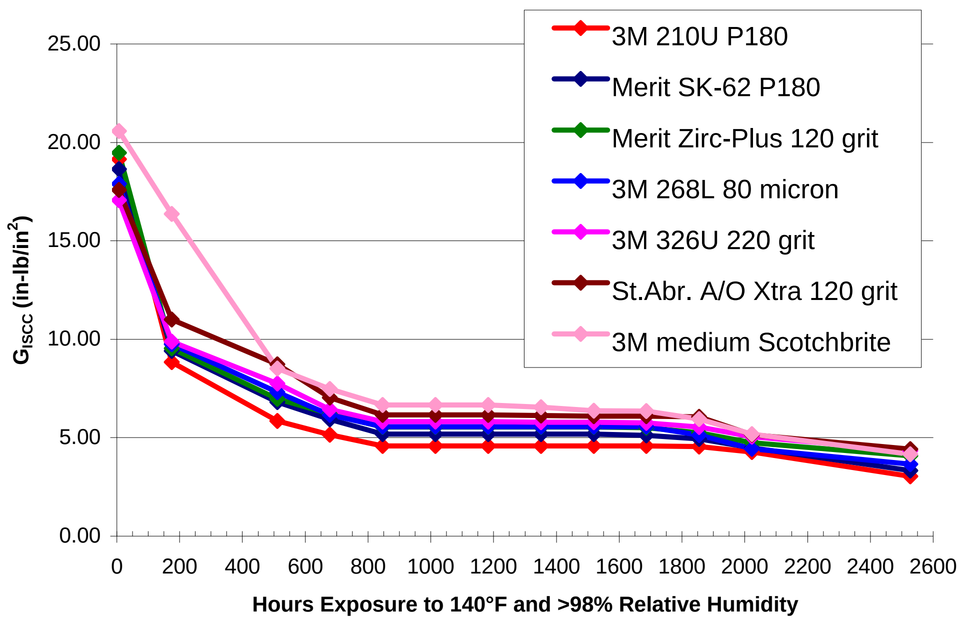


Figure 4.3-3 Environment Crack Extension Force for Abrasive Media Variation Study

Table 4.3-3 Double Cantilever Beam Results Summary

No.	Surface Preparation	Initial Crack Length (in)	5-week Exposure		15-week Exposure		Percent Cohesive Failure
			Crack Length (in)	G_{Iscc} (in-lb/in^2)	Crack Length (in)	G_{Iscc} (in-lb/in^2)	
1	3M 210U-P180	3.05	4.59	4.25	5.18	2.69	40
2	Merit SK-62-P180	3.08	4.43	4.85	5.04	2.98	55
3	Merit 120 Zirc-Plus	3.04	4.34	5.20	4.75	3.74	83
4	268L 80um 5"disc Type D	3.11	4.34	5.21	4.90	3.31	41
5	3M 326U#220 alumina	3.16	4.28	5.48	4.66	4.00	72
6	StAb A/O Xtra #120 grit	3.13	4.21	5.82	4.64	4.08	62
7	Scotch-Brite™ med. Roloc	2.99	4.12	6.33	4.72	3.82	57

4.3.4 Surface Analysis

ESCA

Aluminum Substrates. An ESCA survey-scan was performed on sample specimens treated with the candidate abrasive media to determine the ability of the media to remove the outer oxide layer and the relative cleanliness of the abraded surface. Data for the sandpaper samples and the solvent-wiped and chemically deoxidized controls are shown in Table 4.3-4. Raw data are included in the Appendix. The reduction of magnesium and increase of aluminum at the surface between the solvent wiped and abraded samples indicates that the bulk alloy has been exposed. The source of the higher carbon level on the surface of the Scotch-Brite™ -abraded and chemically deoxidized panels cannot be attributed to a specific source from these data alone. Possible sources include organic material from the Scotch-Brite™ pad or excess carbon pickup on a highly activated surface.

Table 4.3-4 Summary ESCA Data for Aluminum Substrates with Different Surface Preparations

No.	Surface Preparation	Atomic %				
		Carbon	Oxygen	Aluminum	Magnesium	Other
---	Solvent Wiped	36.1	34.3	6.2	23.2	0.2
1	3M 210U-P180	16.2	45.0	35.7	1.7	1.3
2	Merit SK-62-P180	14.5	45.1	36.8	2.0	1.6
3	Merit 120 Zirc-Plus	12.9	43.7	38.5	2.4	2.6
4	268L 80mm 5-in disc Type D	15.6	44.6	36.6	2.4	0.7
5	3M 326U #220 alumina	13.6	44.8	37.5	2.4	1.6
6	StAb A/O Xtra #120 grit	13.9	44.0	38.1	2.5	1.5
7	Scotch-Brite™ med. Roloc	29.2	35.6	32.9	0.8	1.4
---	Chemical Deoxidation	25.8	36.2	24.9	0.6	11.5

Abrasive Media. ESCA was performed on abrasive media numbers 1, 2, 6, and 7 before and after use to determine changes, if any, to the media. The only significant difference between the before and after ESCA numbers was a slight pickup of aluminum and/or magnesium, which would be expected. Raw data for the abrasive media ESCA are included in the Appendix.

Scanning Electron Micrography (SEM)

Aluminum Substrates. SEM photomicrographs were taken of each sample to observe the surface morphology. Representative photomicrographs at 50X and 500X are shown in Figure 4.3-4. The following observations were made from the photomicrographs and Energy Dispersive X-ray Analyses (EDX) that were provided:

- The difference in gross morphology due to preparation method (die grinder vs. random orbital sander) is evident at 50X (samples 1, 2, 4, and 5 vs. samples 3, 6, and 7).
- #1 (3M 210U-P180) sandpaper may be degrading and burnishing the substrate.
- #3 (Merit 120 Zirc-Plus) showed no apparent zirconia contamination, either by EDX or ESCA, even though the hardness of zirconia (6.5 Mohs, 1160 Knoop) is lower than that of alumina (9 Mohs, 2100 Knoop) [for reference, diamond is 10 Mohs and 7000 Knoop].[8] It is the only zirconia medium included in this study; all others are alumina. This surface preparation has done well in performance tests in the past.
- #4 (268 80um 5:disc Type D) has finer features but more loose "junk" on the surface.
- #5 (3M 326U #220 alumina) exhibited definite burnishing.
- Iron (which was not detected with ESCA) was detected by EDX in some of the samples, most notably #1.

Abrasive Media. SEM photomicrographs were also taken of all the candidate media before and after use. Summary photos are shown in Figure 4.3-5. The following observations were made:

- Density of abrasive grit varies greatly between media.
- Embedding of aluminum particles was seen in numbers 1, 3, 4, and 6 after use.
- Grit high points were damaged or broken down during use in numbers 2, 3, and 6.
- Some binders exhibited cracking before and/or after use.
- #4 exhibited holes or bubbles in the binder which were more apparent after use.

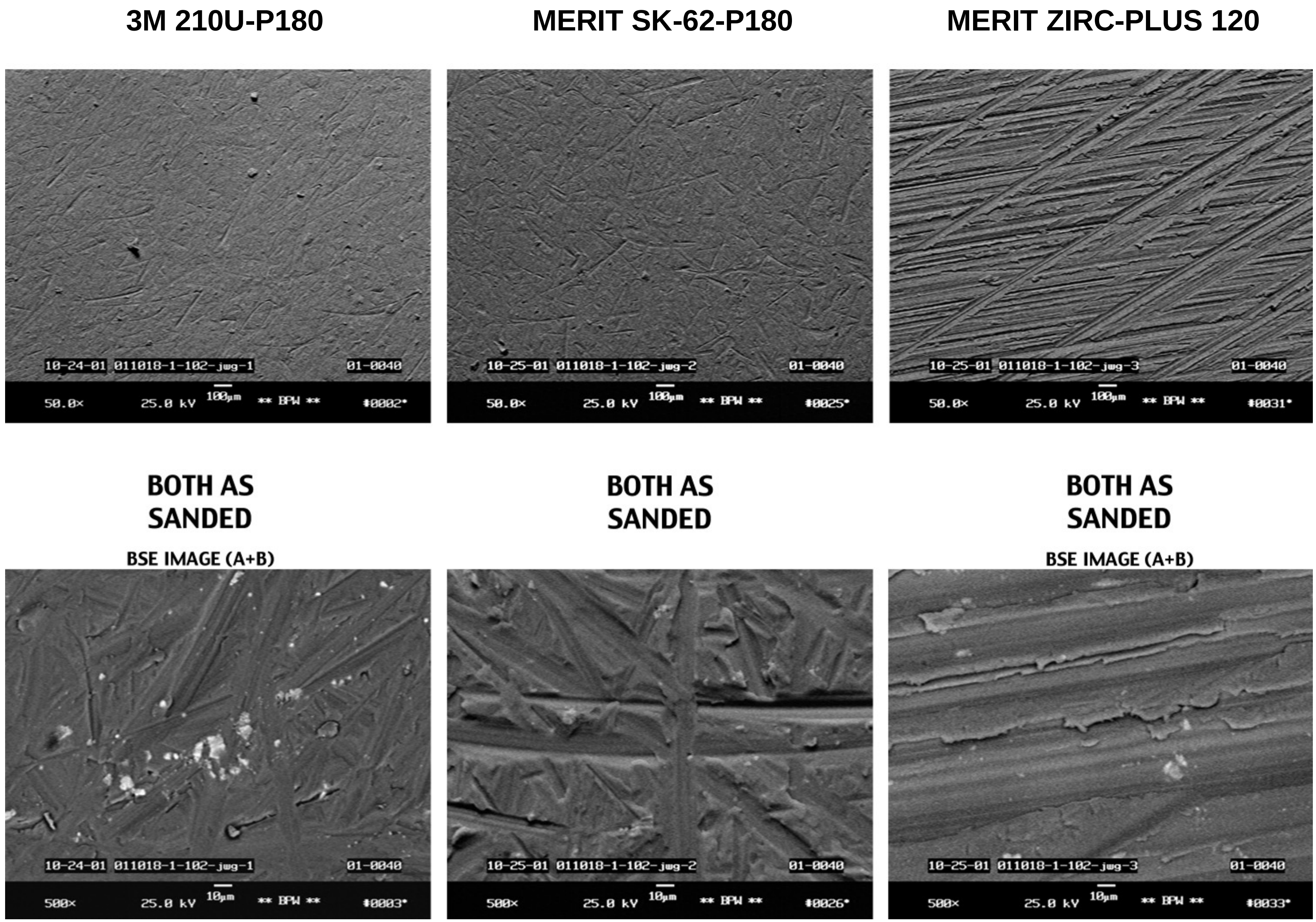
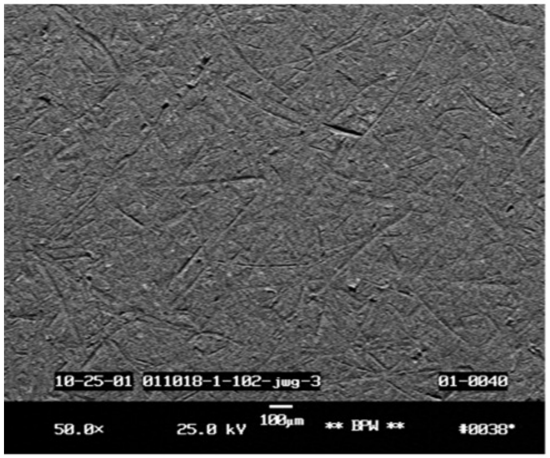
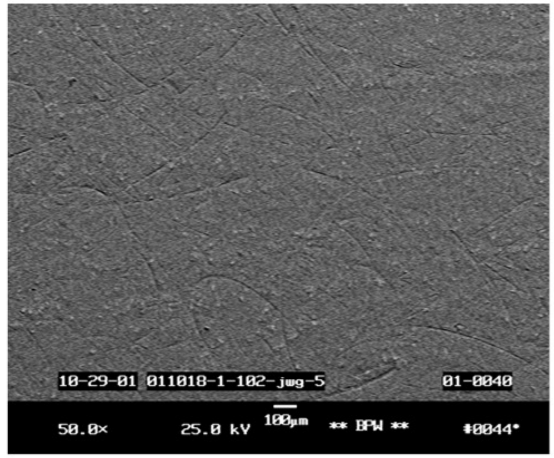
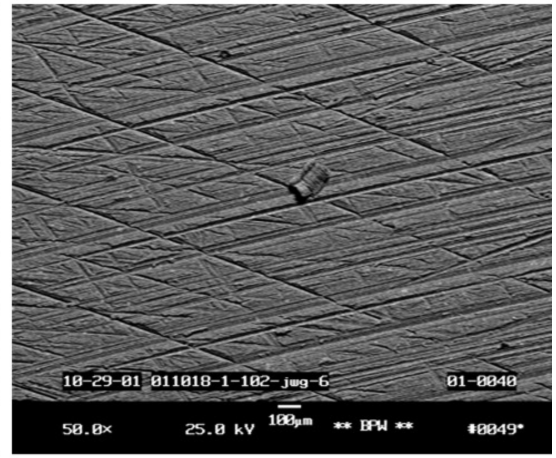


Figure 4.3-4 SEM Photos of Aluminum Substrates After Deoxidation with Various Abrasive Media

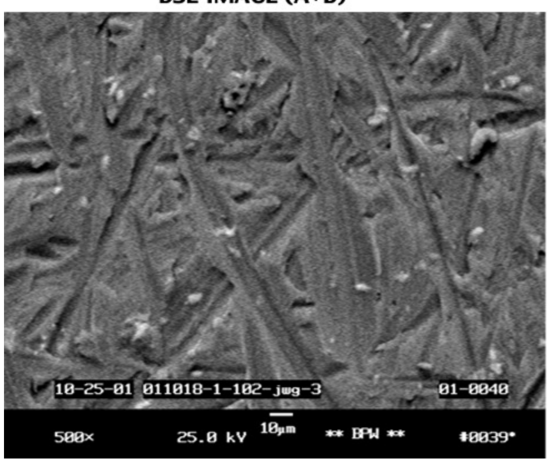
3M 268L 80 MICRON 5-IN | **3M 326U #220 ALUMINA** | **ST.AB. A/O XTRA 120 GRIT**



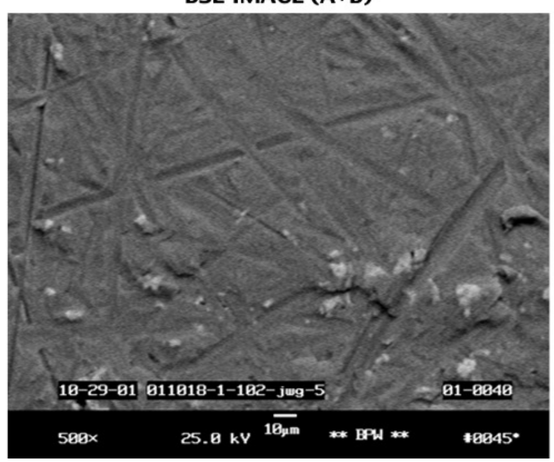




BOTH AS SANDED
BSE IMAGE (A+B)



BOTH AS SANDED
BSE IMAGE (A+B)



BOTH AS SANDED
BSE IMAGE (A+B)

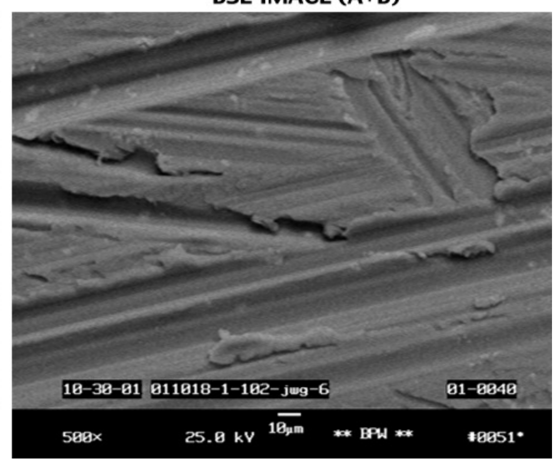


Figure 4.3-4 SEM Photos of Aluminum Substrates After Deoxidation with Various Abrasive Media (cont'd.)

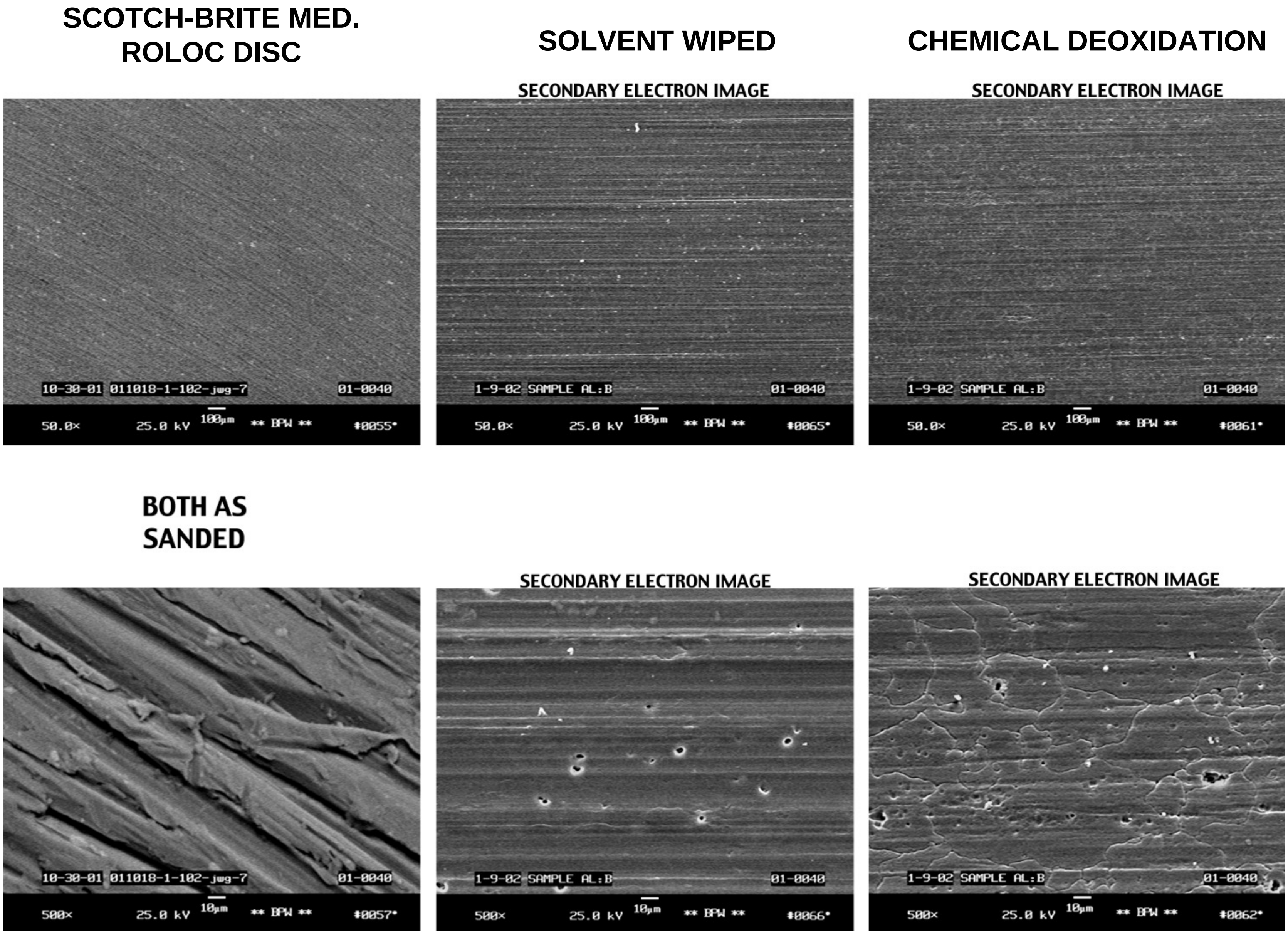


Figure 4.3-4 SEM Photos of Aluminum Substrates After Deoxidation with Various Abrasive Media (cont'd.)

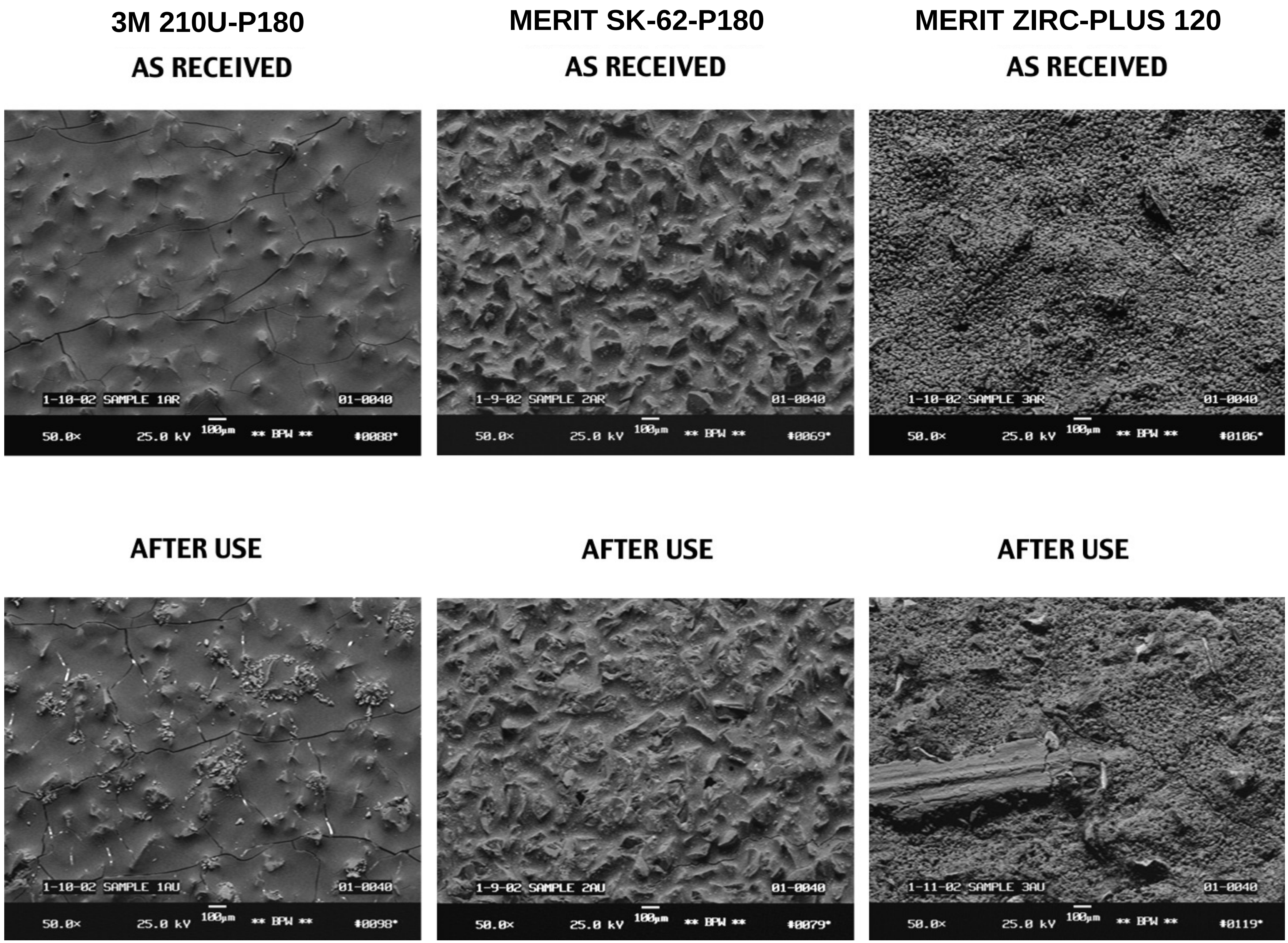


Figure 4.3-5 SEM Photos of Abrasive Media Before and After Use

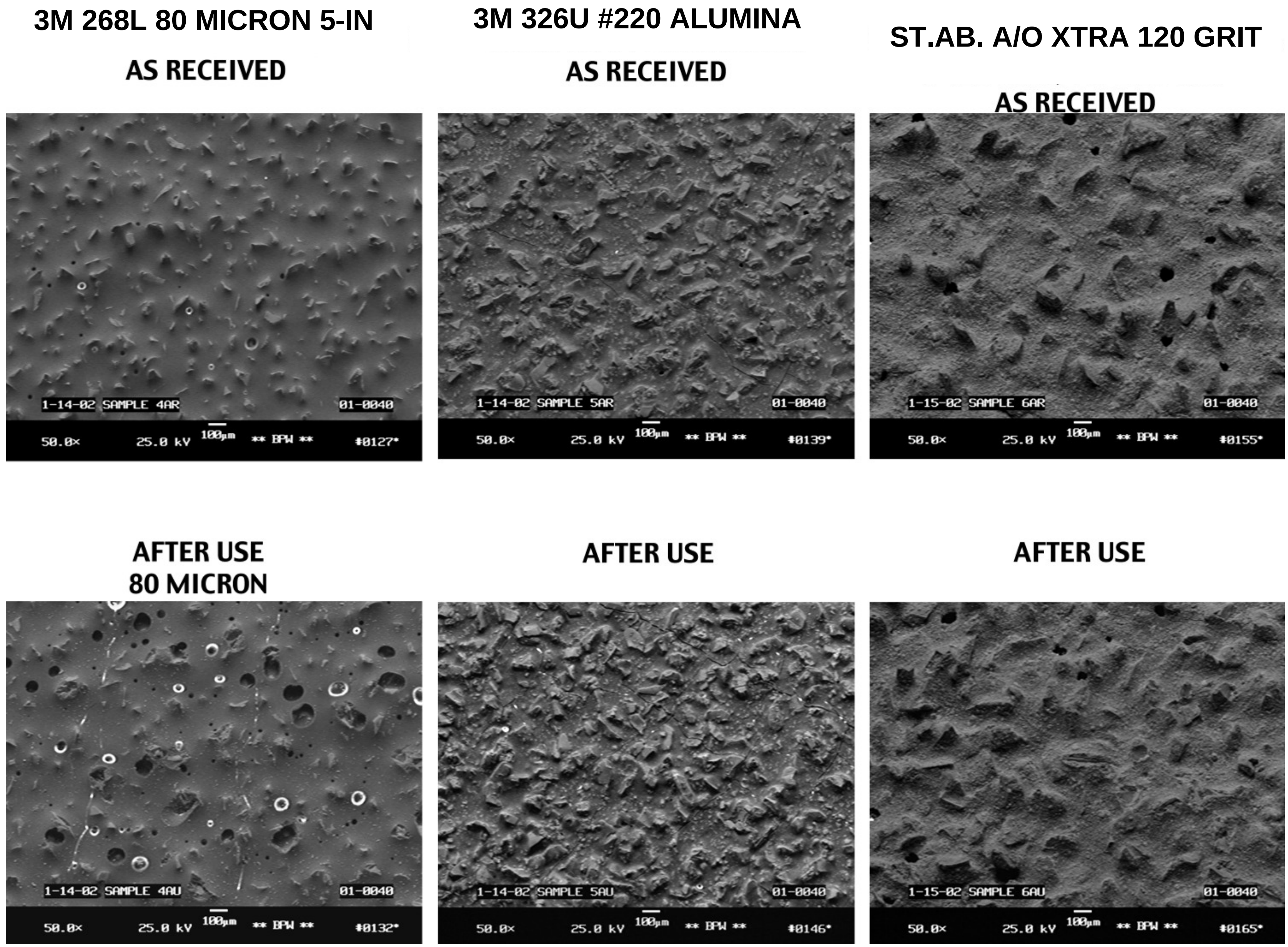


Figure 4.3-5 SEM Photos of Abrasive Media Before and After Use (cont'd.)

SCOTCH-BRITE MED.
ROLOC DISC

AS RECEIVED

AFTER USE

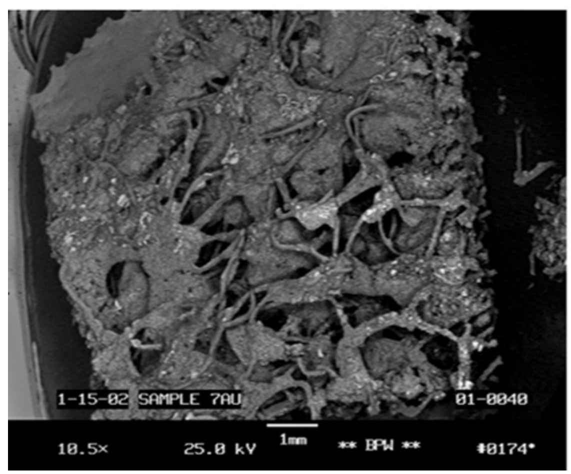


Figure 4.3-5 SEM Photos of Abrasive Media Before and After Use (cont'd.)

Surface Roughness

The surface roughness of each of the abraded aluminum samples was measured using a Wyko NT2000 Optical Profiler. This equipment uses vertical scanning interferometry to measure the profile of surfaces. It has a 10 x 0.5 objective and reports roughness values in μin. Table 4.3-5 shows a comparison of roughness values for the test matrix. Figure 4.3-6 shows the results of this analysis with a key to the different roughness values reported.

The differences in abrasion pattern seen in the SEM photomicrographs between the random orbital sander (numbers 1, 2, 4, and 5) and the die grinder (numbers 3, 6, and 7) are also very apparent in the surface maps shown in Figure 4.3-6. Also interesting is the similarity in roughness values between similar media and tools, i.e. numbers 1, 2, and 4 (random orbital sander), and numbers 6 and 7 (die grinder). Number 3 (Merit Zirc-Plus 120 grit) had an unusually deep profile, possibly due to the zirconia grit, as number 6 is also120 grit (alumina). Number 5 had an unusually low profile, probably due to the fact that the paper is designed for use with wood, not metal.

Table 4.3-5 Summary of Aluminum Panel Roughness Values

	Sample #						
Value	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Ra	28.06	32.31	94.91	35.91	16.96	52.88	59.14
Rp	370.16	438.82	712.57	391.68	180.80	300.01	218.18
Rq	38.07	44.29	127.94	48.21	22.50	67.55	77.52
Rt	793.27	835.00	1361.52	793.89	353.30	876.96	568.31
Rv	-423.11	-396.17	-648.95	-402.20	-172.50	-576.95	-350.13

Note: Die grinder sample columns are shaded.

KEY:

Ra, Roughness Average: The arithmetic average height calculated over the entire array.
Rp, Maximum Profile Peak Height: The distance between the mean line and the highest point over the evaluation length.
Rq, Root Mean Square: The root mean square average height calculated over the entire measured array.
Rt, Maximum Profile Height: The distance between the highest and lowest points over the evaluation length.
Rv, Maximum Profile Valley Depth: The distance between the mean line and the lowest valley over the evaluation length.

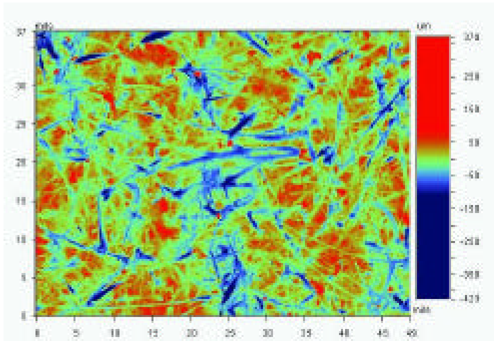
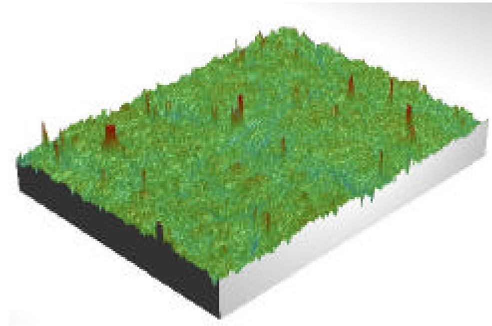
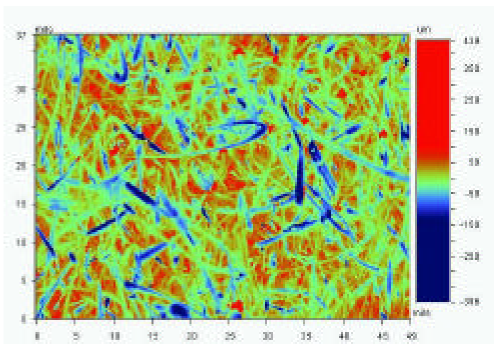
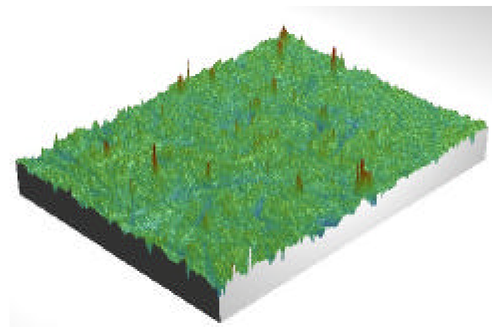
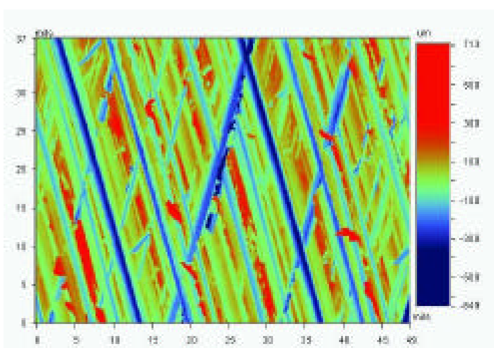
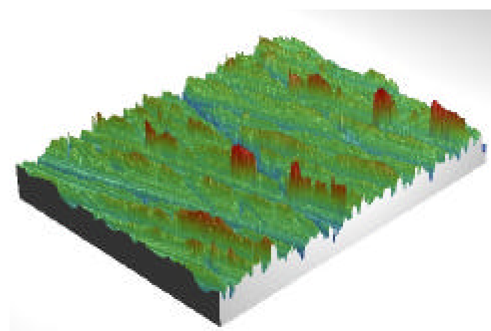
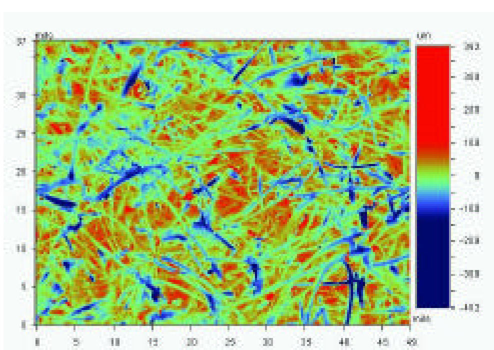
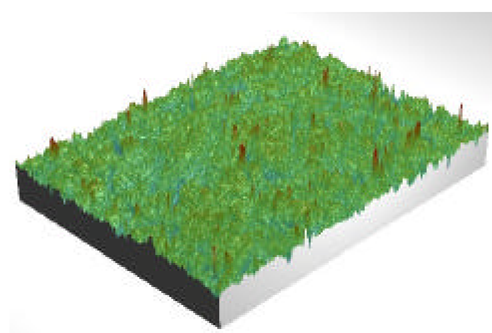
3M 210U P180 Ra 28.06 Rp 370.16 Rq 38.07 Rt 793.27 Rv -423.11		
Merit SK-62-P180 Ra 32.31 Rp 438.82 Rq 44.29 Rt 835.00 Rv -396.17		
Merit 120 Zirc-Plus Ra 94.91 Rp 712.57 Rq 127.94 Rt 1361.52 Rv -648.95		
3M 268L 80 micron Ra 35.91 Rp 391.68 Rq 48.21 Rt 793.89 Rv -402.20		

Figure 4.3-6 Surface Profile Results for Aluminum Substrates Abraded with Various Media

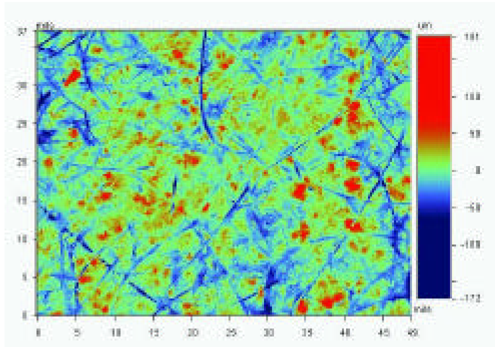
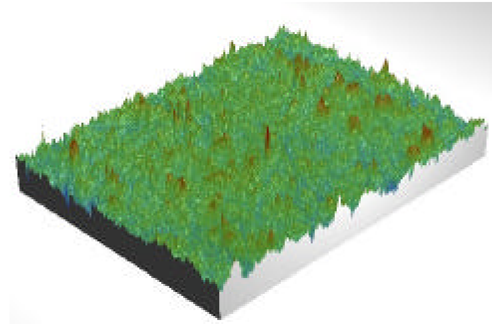
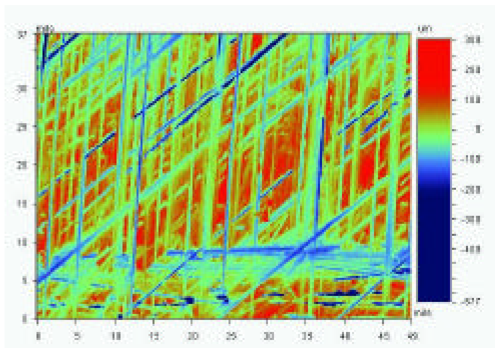
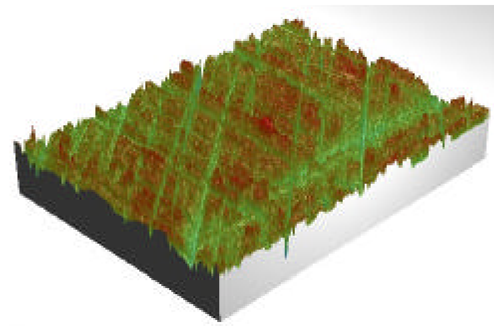
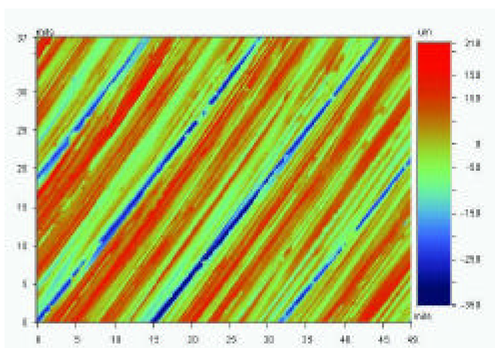
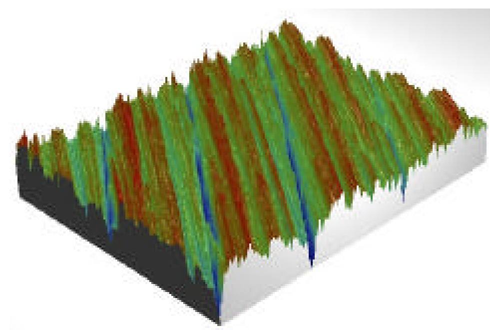
3M 326U #220 alumina Ra 16.96 Rp 180.80 Rq 22.50 Rt 353.30 Rv -172.50		
Standard Abrasives A/O Xtra, 120 grit Ra 52.88 Rp 300.01 Rq 67.55 Rt 876.96 Rv -576.95		
Scotch-Brite Medium Roloc Disc Ra 59.14 Rp 218.18 Rq 77.52 Rt 568.31 Rv -350.13		

Figure 4.3-6 Surface Profile Results for Aluminum Substrates Abraded with Various Media (cont'd.)

4.3.5 Sanding Temperature Study

Thermocouples were attached to aluminum samples during and after sanding to determine the temperature change of the substrate. Table 4.3-6 shows the test matrix and Figure 4.3-7 shows the measured temperature of the aluminum substrate. Thermocouple 1 was taped to the center of the back of the 6 in x 6 in x 0.020 in specimen, and thermocouple 2 was placed between the aluminum specimen and tool immediately after sanding/grinding. Samples 1, 2, 4, and 5 (random orbital sander) were sanded for 2 minutes using a cross-coat technique in a typical

wedge test specimen preparation. Samples 3, 6, and 7 were ground for 1 cross-coat in a typical wedge test specimen preparation.

Table 4.3-6 Sanding Temperature Matrix

Sample No.	Sandpaper				Tool			
	Mfgr.	Type	Grit	Diameter	Mfgr.	Type	Speed	Diameter
1	3M	210U	P180A	5 inch	DeWalt	ROS	10500 rpm	5 inch
2	Merit	A/O SK-62	180	5 inch	DeWalt	ROS	10500 rpm	5 inch
3	Merit	Zirc Plus	120	3 inch	Myton	D.G.	22000 rpm	3 inch
4	3M	268L	60 u	5 inch	DeWalt	ROS	10500 rpm	5 inch
5	3M	326U	220	5 inch	DeWalt	ROS	10500 rpm	5 inch
6	Std. Abr.	A/O Xtra	120	3 inch	Florida	D.G.	25000 rpm	2 inch
7	3M	Scotchbrite	medium	2 inch	Florida	D.G.	25000 rpm	2 inch

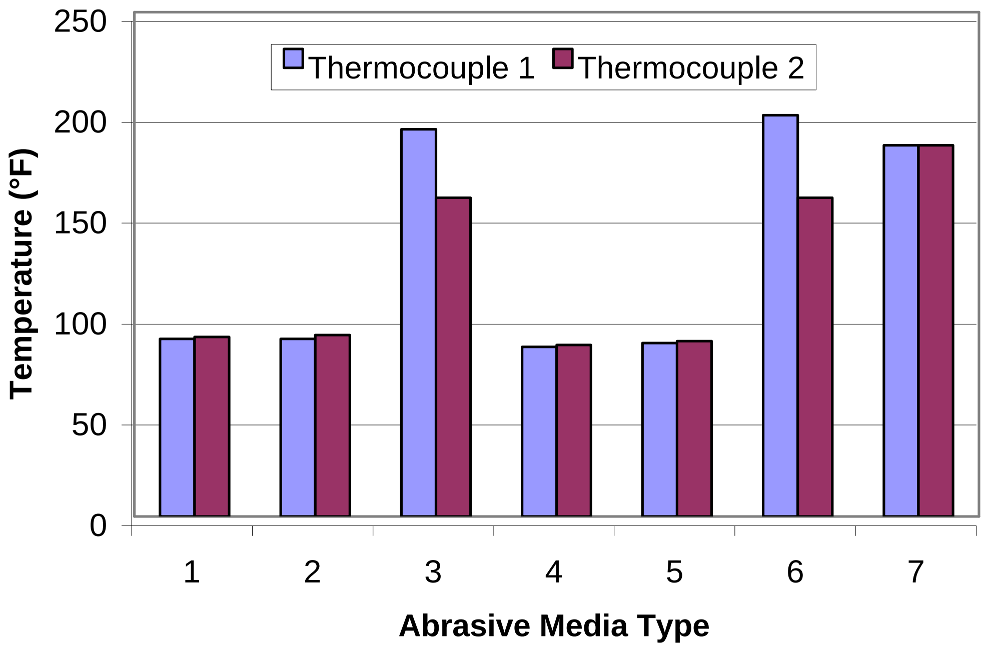


Figure 4.3-7 Measured Temperatures for Aluminum Substrates Abraded with Various Media

Again, there is a clear difference in the samples abraded using the die grinder and those abraded using a random orbital sander. However, there has not been a good technique to date to understand the connection between surface temperature/overheating and bond performance.

5 Hybrid Development

5.1 Summary

Optimum cure parameters were investigated for previously developed hybrid primer formulations. Panels bonded with the hybrid primer under investigation, when precured at room temperature for a minimum of 45 minutes, form films that do not exhibit solvent popping or other apparent physical imperfections. Acceptable levels of pencil hardness (H, per BMS 10-79) and impact resistance can be expected after 24 hour at room temperature or 120°F. Acceptable levels of durability, measured by impact and wedge testing, have been achieved with an initial cure at 72°F for one hour followed by one hour at 120°F and one hour at 150°F. These values are equivalent to values that were previously reported and attained after curing at room temperature for seven days, applying paste adhesive, and bonding. Other parameters tested include water addition, mixing order, application of adhesive to uncured primer, and addition of nonchromated inhibitors.

5.2 Background

The focus of this task was to develop and optimize a rapid-cure process for a hybrid system which was formulated to take on the functional roles of both the surface preparation and the adhesive bond primer. To enable such a technology, components of both the sol-gel chemistry and primer chemistry are incorporated into the hybrid coating system. Implementation of such a coating would reduce the amount of hazardous materials (chromates, acids, and bases) used both in the conversion coating process and the primer application. Additionally, use of a single coating would save time and cost in the application process for metal-bond repairs. The initial application is targeted at use with paste adhesive systems. The hybrid formulation must be waterborne, ambient or low-temperature curing, and provide acceptable adhesion and durability when used with typical aerospace epoxy paste adhesive systems.

Discussions with representatives of the Naval Aviation Depots and Air Force Logistics Centers indicate extensive interest in the use of an ambient-cured system. Interest was also expressed in systems with elevated cure up to 200°F to speed repair/production rates. In many depot repair scenarios, heat cannot be applied to the structural hardware or it may result in more damage. Therefore, two-part paste adhesive systems that can be cured at ambient or slightly elevated temperatures are often employed for repair. However, there is currently no acceptable bond primer that can also be cured at ambient temperatures and achieve an acceptable level of durability performance. Therefore, typically no bond primer is used, limiting the expected lifetime of the repair due to moisture ingression to the interface, corrosion, and eventual disbond. Repeated repairs of the same hardware are often the result; this can add significant cost to the lifecycle cost of the vehicle.

There is also significant interest in having a completely nonchromated ambient-cure system available for locations where the use of chromium and other toxic chemicals is restricted.

5.3 Test Results

5.3.1 Curing Temperature Characteristics

A sample of hybrid primer formulation RS-HY was evaluated on a Fisher-Johns melting point apparatus to determine cure behavior at temperatures less than 200°F. RS-HY hybrid primer placed on the hot stage of a Fisher-Johns melting point apparatus preheated to 104°F resulted in bubbling of the resin with the formation of craters and bubbles upon cooling. A coating pre-dried at room temperature for 15 minutes produced a smooth film.

5.3.2 Performance Testing of Initial Formulation

The primer was also evaluated for crack extension (wedge test), GE impact, and impact adhesion after curing after exposure to 180°F for varying lengths of time. Coatings for each set of wedge test specimens were applied to two 6 in x 6 in x 0.125 in 2024T-3 aluminum panels grit-blasted with aluminum oxide. Panels were exposed to elevated temperature ten minutes after application and were tacky to the touch. Coatings were allowed to cure at 180°F for one half, one, and two hours. After an additional seven days at room temperature, Hysol 9309.3 NA paste adhesive was applied over glass scrim, using a notched trowel to control the bondline thickness between the coated panels. The sandwiched parts were cured in accordance with BMS5-109 by bagging under vacuum at room temperature for seven days and then were cut into five test specimens. Crack growth was measured after initiating the crack with a wedge under ambient conditions followed by seven days exposure to 120°F and 98% RH. Impact adhesion and GE impact specimens were prepared from 4 in x 6 in grit-blasted panels of 0.020-in 2024T-0. Impact adhesion panels were tested at 40 inch-lbs. The panels were tested after seven days exposure under the same conditions as the other test panels.

Coatings on wedge test, GE impact, and impact adhesion panels cured at 180°F resulted in a rippled texture with solvent popping and a dull gloss. Wedge test panels had crack growths significantly in excess of the desired range. GE impact test results for one and two-hour cures failed 60% elongation but passed 40%. The panel cured for one half hour failed 10% elongation. All panels failed reverse impact testing.

5.3.3 Water Addition

Three additional batches were run, varying the amount of additional water, to optimize viscosity and subsequent handling behavior. Addition of 40% water based on the total weight of primer ingredients gave the best handling characteristics with satisfactory GE impact and reverse impact test results.

5.3.4 Cure Parameter Test Matrix

As a result of the preceding tests, a full factorial test matrix was conducted to evaluate effects of room-temperature dry time for 45 and 90 minutes prior to cure at 120° and 200°F for 15 and 30 minutes. Panels prepared with the preferred process developed from this information were then monitored for changes in pencil hardness, GE impact, direct and reverse impact, and impact adhesion as a function of time at elevated temperature compared to specimens cured at room temperature.

Because of the poor test results from panels immediately cured at 180°F and the cure behavior on the melting point apparatus, it was hypothesized that an extended room-temperature drying time should improve test results. Statistical evaluation of the test results reported in Table 5.3-1 indicates that the best results would be obtained if all factors were held at the minimum values tested. Solvent popping was not observed when panels were held at room temperature a minimum of 45 minutes.

Table 5.3-1 Effect of Cure Parameters on Impact Performance

Specimen	Dry time at RT (minutes)	Bake temp (°F)	Bake time (minutes)	GE impact (% elongation)	Reverse/direct impact
A	45	120	30	60	Pass
B	90	200	30	Fail	Fail
G	45	200	15	Fail	Fail
D	90	120	30	60	Fail
E	90	120	15	60	Pass
F	90	200	15	Fail	Fail
C	45	120	15	60	Pass
H	45	200	30	20	Fail

Further refinement of factor settings was made possible by analysis of performance as a function of drying time at room temperature and 120°F after an initial one hour at room temperature. The results from this series of tests, reported in Table 5.3-2, indicate that acceptable impact resistance can be obtained after curing for 124 hours at room temperature or after 24 hours at 120°F. The table also shows that films attain a pencil hardness of 3H after curing 24 hours at room temperature, 5H at 120°F, and 7H after curing 168 hours at room temperature or 120°F. The minimum hardness requirement for Boeing BMS10-79 epoxy primer is H.

Table 5.3-2 Impact Performance and Hardness as a Function of Cure Time at Room Temperature and 120°F

Cure time	Room temperature			120°F		
	Hardness	GE impact	Rev/direct impact	Hardness	GE impact	Rev/direct impact
15 min	-	-	-	3B	Fail	Fail
30 min	-	-	-	B	Fail	Fail
1 hr	-	-	-	F	Fail	Fail
1.5 hr	-	-	-	2H	Fail	Fail
2 hr	-	-	-	2H	Fail	Fail
2.5 hr	2B	Fail	Fail	2H	Fail	Fail
24 hr	3H	40	Pass/Fail	5H	60	Pass
124 hr	5H	60	Pass	5H	60	Pass
168 hr	7H	60	Pass	7H	60	Pass

5.3.5 Application of Adhesive to Uncured Primer

At this point, application of adhesive to uncured (or partially cured) hybrid primer had not been investigated. To determine if this method might work, hybrid primer was applied to wedge test adherends and cured for four hours at room temperature to give a 1-mil film. Adherends were then bonded and compared to those with hybrid primer which were cured for an initial hour at room temperature followed by three hours at 120°F prior to bonding. Additional panels were evaluated after curing 24 hours at room temperature and at 120°F.

Wedge test specimens prepared by applying adhesive to uncured hybrid primer in accordance with Table 5.3-3 produced crack lengths ranging from 0.58 to 1.12 inches after four weeks exposure to 98% RH at 120°F.

Table 5.3-3 Wedge Test Specimens Prepared by Applying Adhesive to Partially Cured Hybrid Primer

Specimen Identification	4-week Crack Growth[1]	% Cohesive Failure[1]	Cure parameters of primer
81-8A	0.95	52	4 hr 72°F
81-8B	0.66	96	1 hr 72F plus 3 hr 120°F
81-9A	0.94	63	24 hr 72°F
81-9B	0.80	98	24 hr 120°F

1) Average for 5 specimens

5.3.6 Accelerated Cure

Based on results from these tests, temperatures up to 200°F with different exposure times were also evaluated to further accelerate the cure process.

Test results for combinations of exposure times and higher temperatures are presented in Table 5.3-4. Impact, pencil hardness, and wedge test data indicate that acceptable results are achieved with a cure cycle consisting of drying the primer at 72°F for one hour, followed by one hour at 120°F, and then one hour at 150°F. The cause of the poor impact performance for the control has not been determined.

Table 5.3-4 Evaluation of Additional Elevated Temperatures

Specimen Identification	1-week Crack Growth[1]	% Coh. Failure[1]	GE impact % elong.	Rev/direct impact	Pencil hardness	Cure parameters
69-RS1	0.65	100	60	Pass	9H	1 hr 72°F, 1 hr 120°F, 1 hr 150°F
69-RS2	0.73	88	60	Pass	9H	1 hr 72°F, 1 hr 120°F, 24 hr 150°F
69-RS3	0.73	98	60	Pass	9H	1 hr 72°F, 1 hr 120°F, 1 hr 200°F
69-RS4	0.83	100	20	Pass/Fail	9H	14 days 72°F

1) Average for 5 specimens

5.3.7 Mixing Order

A number of batches of hybrid primer were also produced based on the 69RS formulation reported in Table 5.3-4, with minor changes to the order of addition of the constituents. These changes were made in an attempt to shorten the mixing procedure and minimize the probability of causing a problem in the final coating. The coatings were subsequently cured at room temperature for one hour, plus 120°F for one hour, plus 150°F for one hour and then bonded at 150°F for two hours. In most cases, the resultant coatings failed GE, reverse and/or direct impact tests. However, one batch passed these tests. Nevertheless, in all cases, wedge test results were low (66-81% cohesive failure) and failed to meet the level of performance previously achieved (90-100% cohesive failure). At this point, it appears that changes in the mixing procedure dramatically influence performance.

5.3.8 Addition of Nonchromated Inhibitors

To determine the effect of nonchromated inhibitors on the hybrid coating, a series of corrosion tests frequently conducted on typical exterior paint systems were carried out. This enabled a direct measurement of the corrosion protective capabilities of the materials. Addition of inhibitors to the hybrid coating may extend the environmental durability of the bondline.

Cerium oxide and Wayncor 204 corrosion inhibitors were individually incorporated at 14% by weight with the 69RS hybrid primer. Both of the inhibited hybrid epoxy-silane primers were applied to deoxidized 2024-T3 panels as well as panels that were sulfuric acid anodized with and without chromate seal. Panels were scribed and tested for salt spray corrosion resistance in accordance with BMS10-72 (3000 hrs, minimum 5% salt spray fog at 95°F, at an incline of 6 degrees from vertical). Two controls were also prepared by incorporating strontium chromate.

Each of the nonchromated primers applied to panels that were only deoxidized corroded on the field of the panel (meaning in the nonscribed area) within 7 days of exposure. Control panels treated with boric acid- sulfuric acid anodizing (BAC5632) with and without a chromate seal did not corrode on the field or 0.125 in beyond the scribe up to 3000 hours. In some cases, the corrosion within the scribe was extensive but not severe enough to fail the salt spray test. The deoxidized panels coated with chromated primer remained free from corrosion on the field and developed minimal corrosion within the scribe.

GE, reverse, and/or direct impact tests consistently passed requirements when the induction period of the mixed ingredients was extended from 30 to 45 minutes. Nevertheless, in all cases, the wedge test performance was low (66-81% cohesive failure) and failed to meet the level of performance previously achieved (90-100% cohesive failure).

It is possible that the epoxy or the curing agent may have been contaminated and resulted in the low degree of cohesive failure. The nonchromated corrosion inhibitors evaluated appear to give some corrosion protection that passes the requirements of the exterior paint (BMS10-72) specification when it is applied to panels that have been boric sulfuric acid anodized. However, when applied as a stand-alone coating over a deoxidized surface, they did not give the corrosion protective capabilities required for exterior protection. Whether the amount of inhibitive behavior was enough to protect the bondline was unclear.

6 Conclusions

This report includes the results of optimization studies conducted to improve the reproducibility and robustness of the sol-gel surface preparations and hybrid primers. Several improvements to the Boegel-EPII materials and processes were identified in this work. For instance, addition of a surfactant can improve the appearance and uniformity of the sol-gel coatings, but is not critical to achieving good performance on these alloys.

Studies indicate that careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Under carefully controlled laboratory conditions, it is possible to yield good performance for many of the abrasive media, but when subjected to conditions that mimic a repair scenario, only a few of the abrasive media gave reproducible performance. Surface contamination on the metal was potentially a result of smeared adhesive, or unacceptable cleaning of the surface.

Testing with various abrasion-based deoxidation methods showed differences in the performance of the bonded specimens during hot/wet exposure of the sol-gel prepared specimens. Systematic studies conducted using various power-assisted tools showed that alumina and zirconia sandpapers can adequately deoxidize, roughen, and activate the surface of 2024-T3 aluminum for application of sol-gel. However, appropriate selection of abrasion media and process parameters must occur to yield acceptable bond strength performance and durability. Different abrasive papers or pads had different characteristics. Some experienced wear and degradation faster than others, and some were more effective at obtaining a uniformly deoxidized surface. The Merit alumina and zirconia abrasive papers were found to give the most satisfactory and reproducible performance of those tested here. The 3M 268L and 210U gave variable performance and require further testing to delineate appropriate process conditions for use. Use of medium coarseness Scotch-Brite™ on a Roloc disc can also yield acceptable results.

In conclusion, the use of Boegel-EPII (AC-130) after solvent cleaning and abrading for aircraft metal bond repairs yields acceptable results under controlled processing conditions. The performance with very specific media and process methods is better than many of the methods in use today, such as paste acid etches, and scuff sand/solvent wiping.

Improvements were made to hybrid bond primer formulations and processes. Hybrid primers formed acceptable films that did not exhibit solvent popping or other apparent physical imperfections. Acceptable levels of pencil hardness and impact resistance were achieved after curing for 24 hours at room temperature or 120°F. Acceptable levels of wedge test durability with paste epoxy adhesives were achieved with an initial cure at 72°F for one hour, followed by one hour at 120°F and one hour at 150°F.

7 References

1. K. Y. Blohowiak, Robert A. Anderson, and Ronald R. Stephenson, "Sol-Gel Technology for Surface Preparation of Metal Alloys for Adhesive Bonding and Sealing Operations," Final Report, Contract Number F33615-95-D-3203, Delivery Order #10, Air Force Research Laboratory, March 2001.

2. a) A.A. Baker and R.J. Chester, "Minimum Surface Treatments for Adhesively Bonded Repairs," Int. J. Adhesion and Adhesives., Vol 12, No. 2, page 74, April 1992. b) M.H. Kuperman and R.E. Horton, Adhesive Bonding of Aluminum Alloys, E.W. Thrall and R.W. Shannon (editors), Marcel Dekker, Inc., New York, page 444, 1985. c) S.S. Saliba, "The Surface Preparation of Aluminum Alloys Using the Phosphoric Acid Containment System for Repair," WL-TR-94-4112, 1994.

3. J.J. Mazza, J.B. Avram, and R.J. Kuhbander, "Grit Blast/Silane (GBS) Aluminum Surface Preparation for Structural Adhesive Bonding," WL-TR-94-4111.

4. ASTM D 3762, "Standard Test Method for Adhesive-Bonded Surface Durability of Aluminum (Wedge Test)." Annual Book of ASTM Standards, Volume 15.06: Adhesives.

5. ASTM D 1002, "Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)." Annual Book of ASTM Standards, Volume 15.06: Adhesives.

6. ASTM D 3167, "Standard Test Method for Floating Roller Peel Resistance of Adhesives." Annual Book of ASTM Standards, Volume 15.06: Adhesives.

7. ASTM D 522, "Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings." Annual Book of ASTM Standards, Volume 06.01.

8. Robert C. Weast, ed., CRC Handbook of Chemistry and Physics, CRC Press, Inc., Boca Raton, FL, 1983, p.F-20.

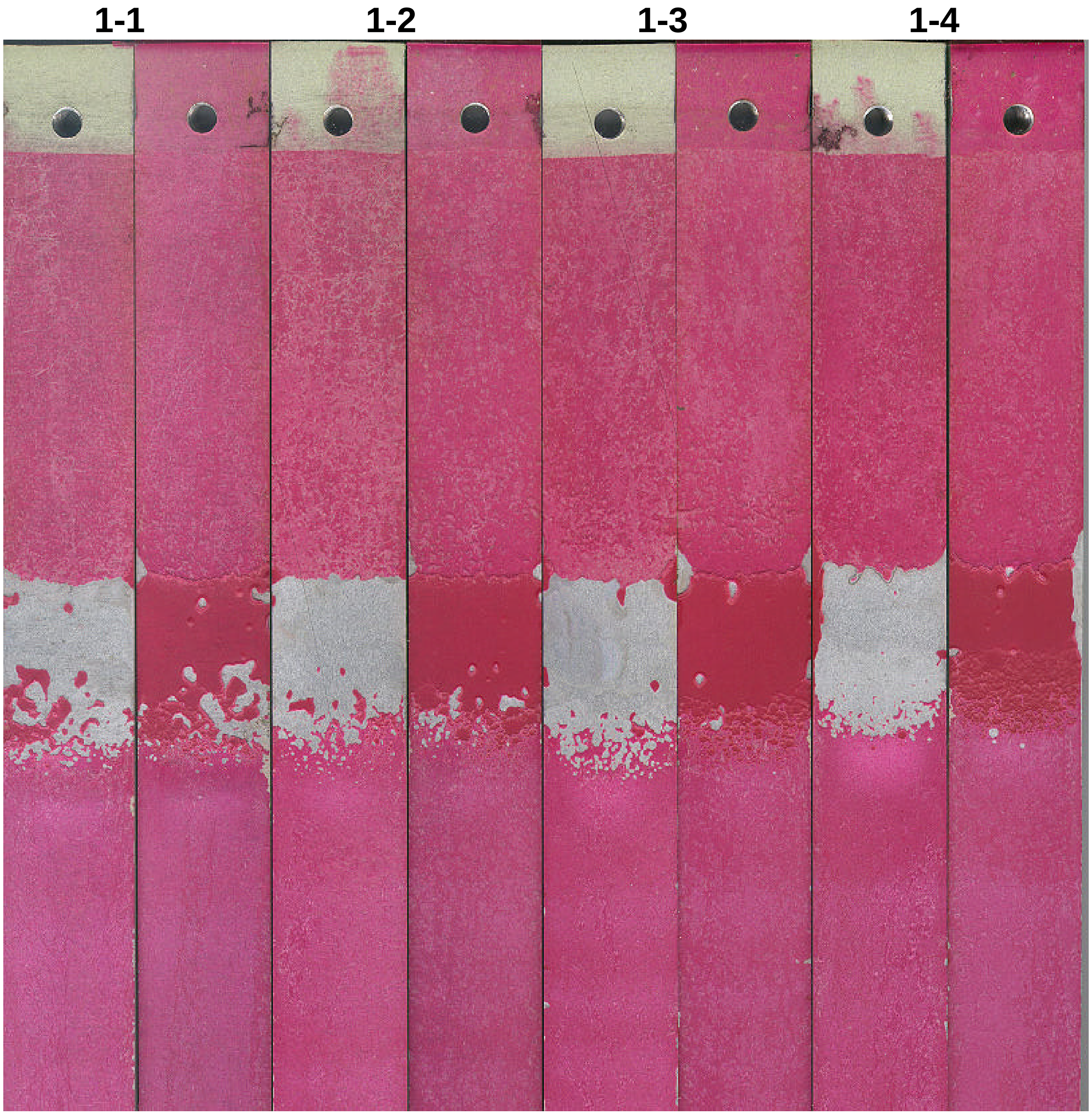
APPENDIX

Contents:

DCB Failure Mode Scans
ESCA Data

Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

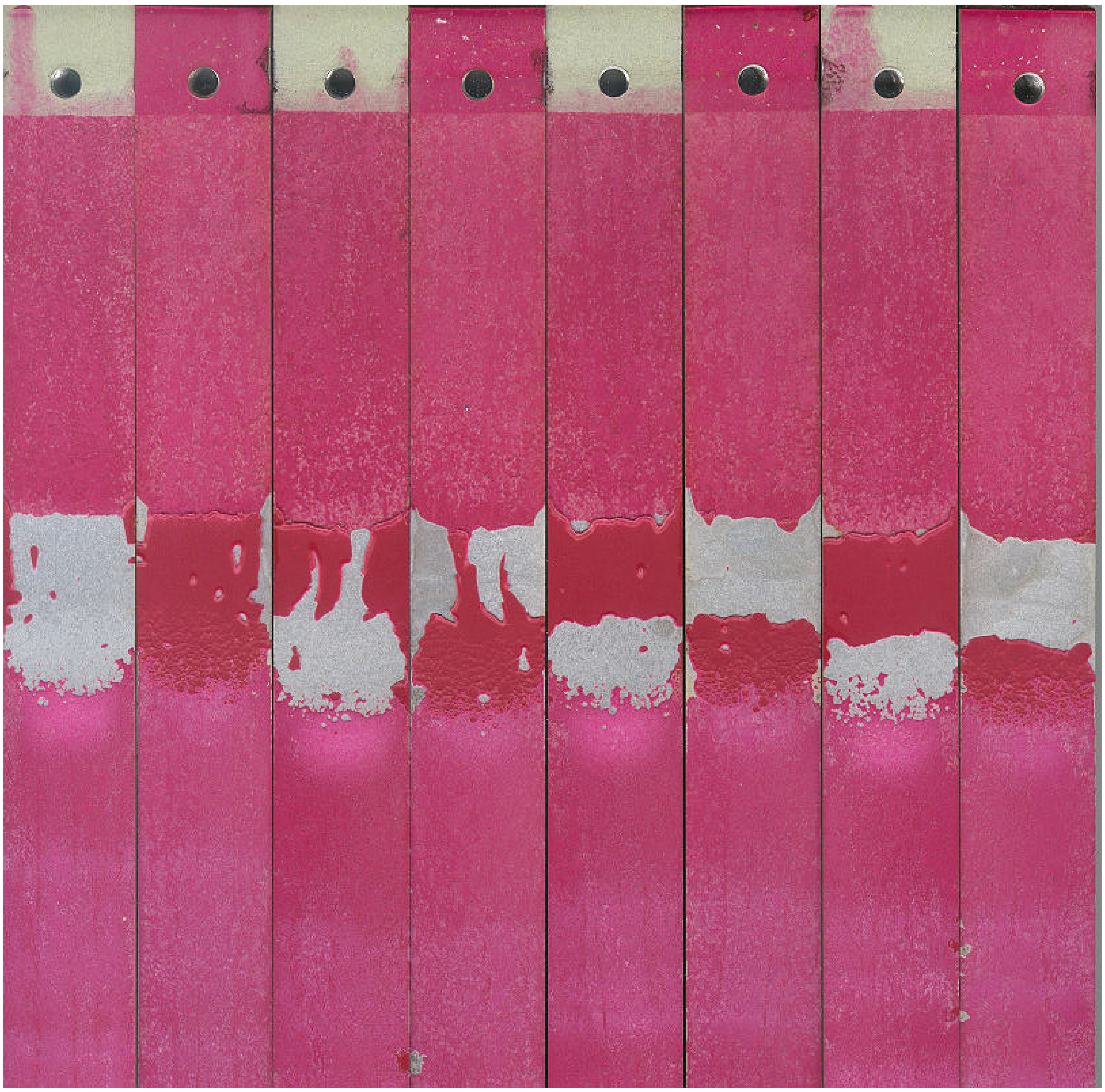
Samples 1-1 through 1-4 (3M 210U P180)



Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

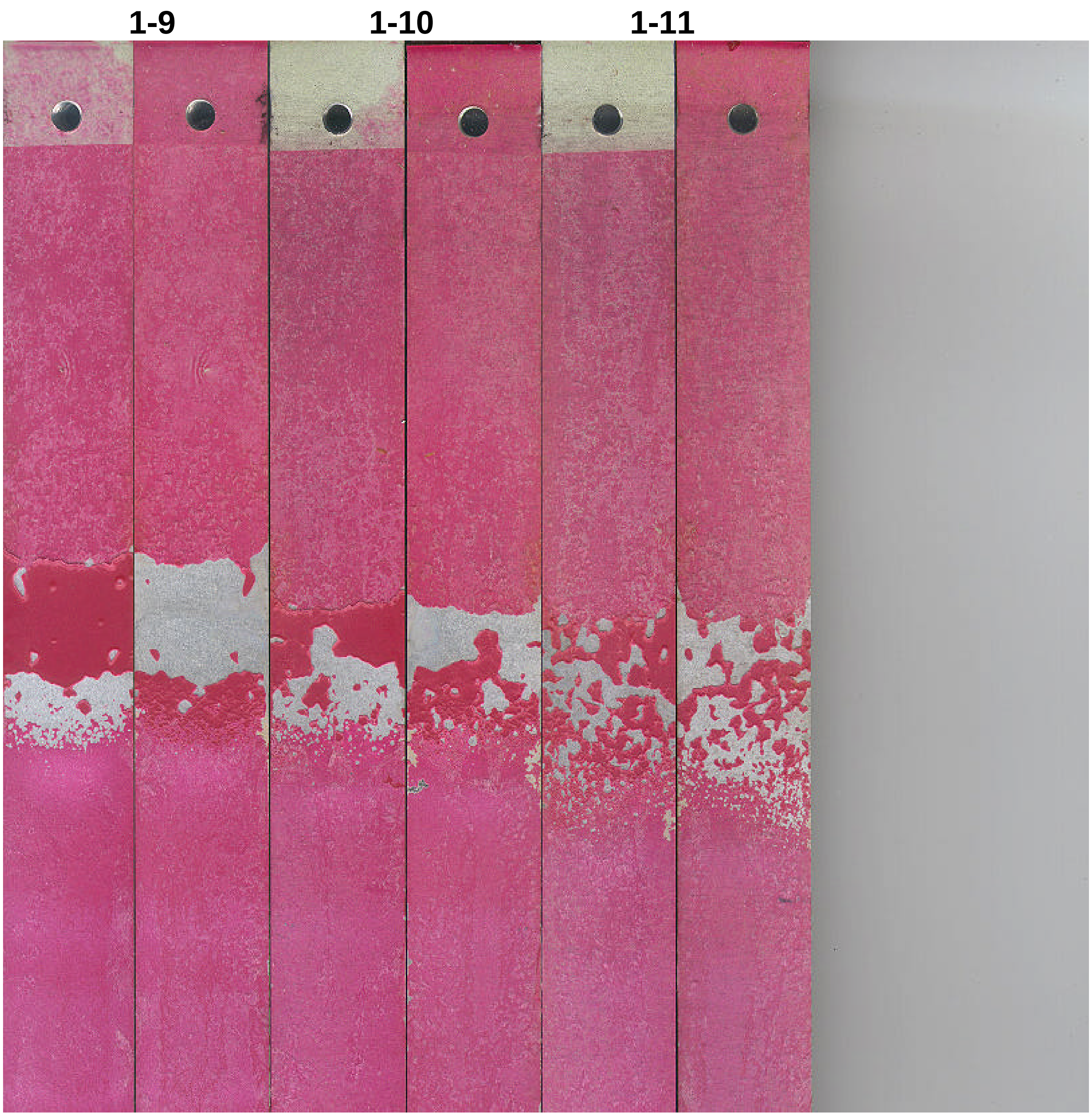
Samples 1-5 through 1-8 (3M 210U P180)

1-5 1-6 1-7 1-8



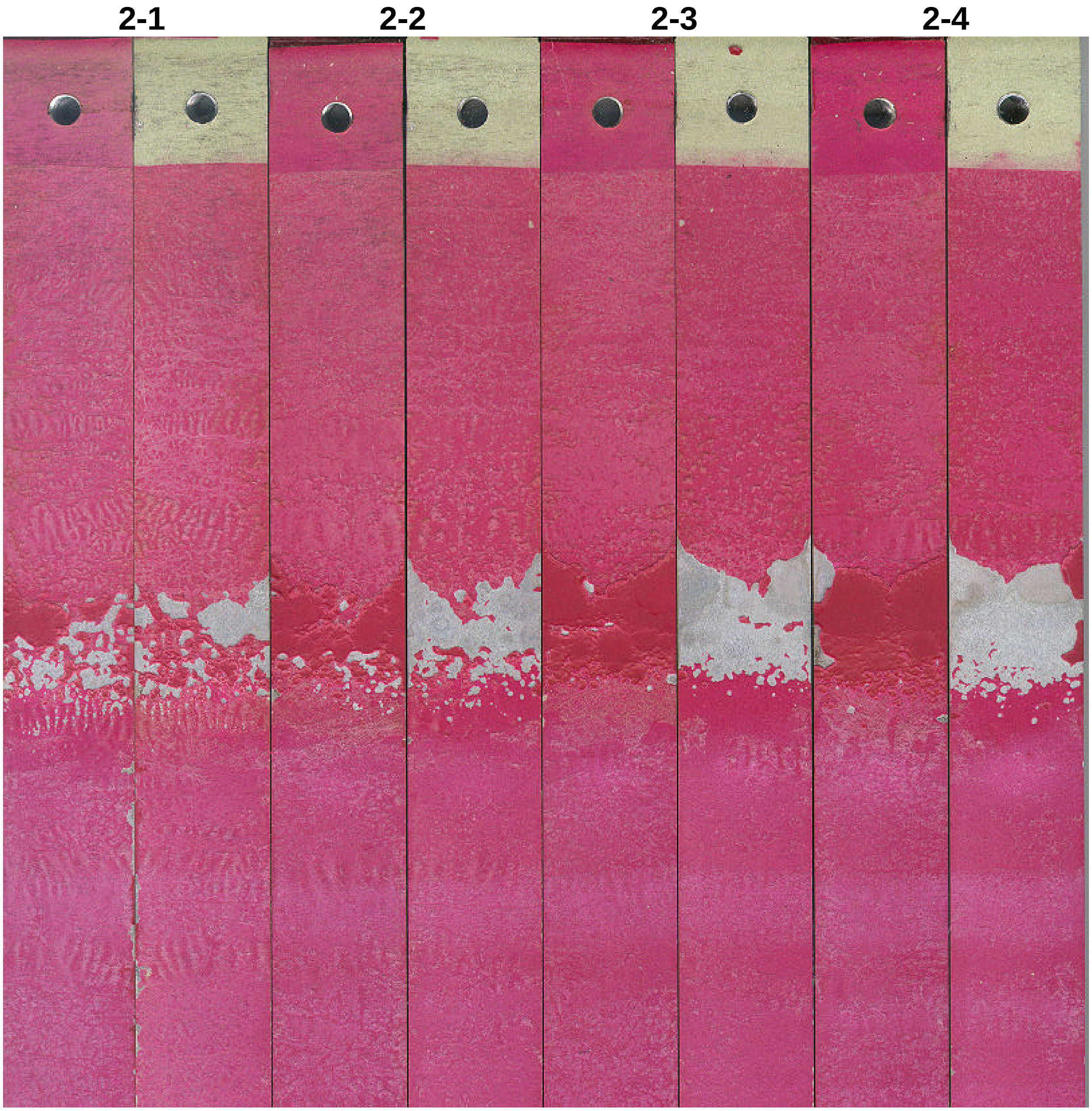
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 1-9 through 1-11 (3M 210U P180)



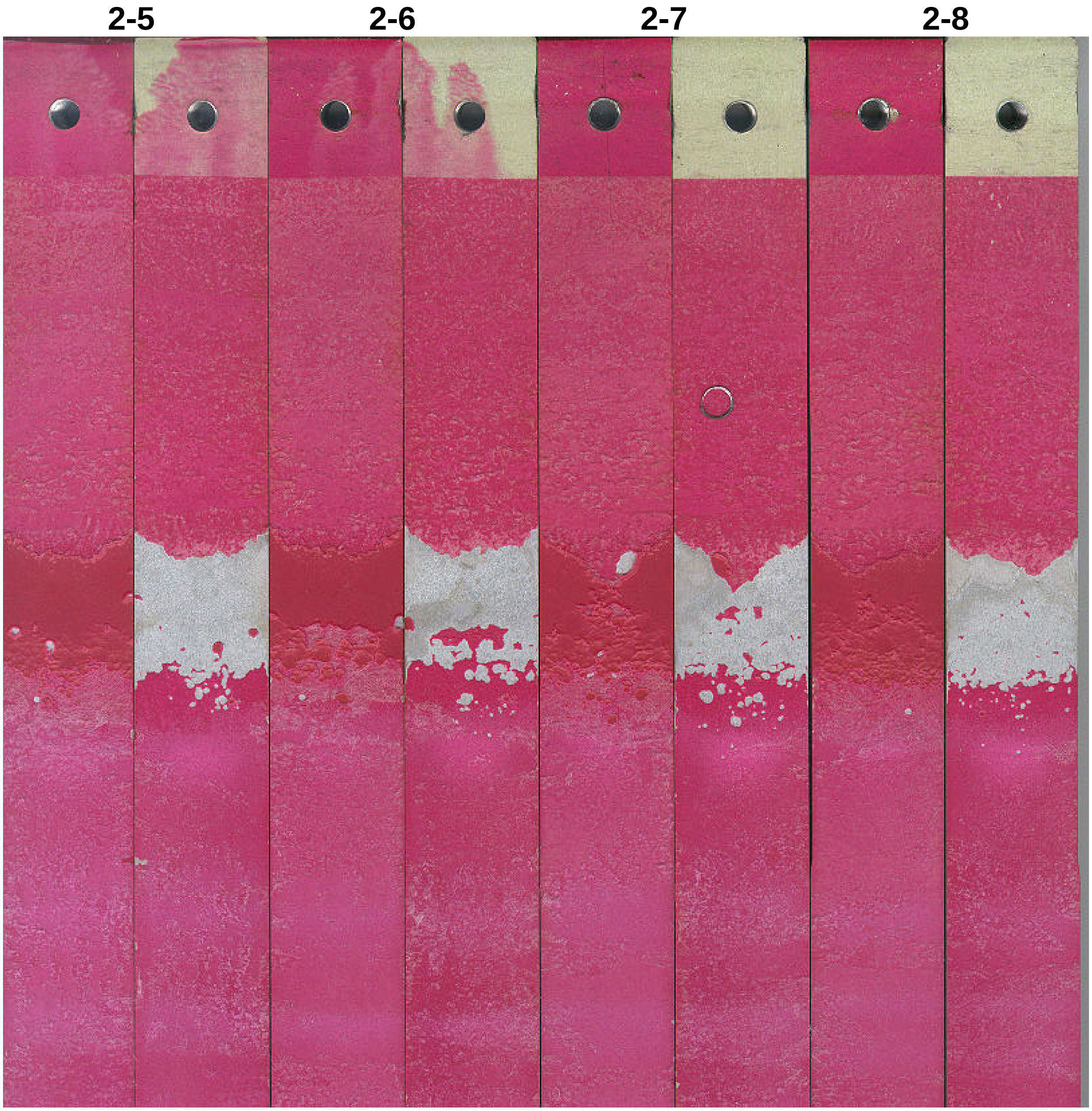
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 2-1 through 2-4 (Merit SK-62-P180)



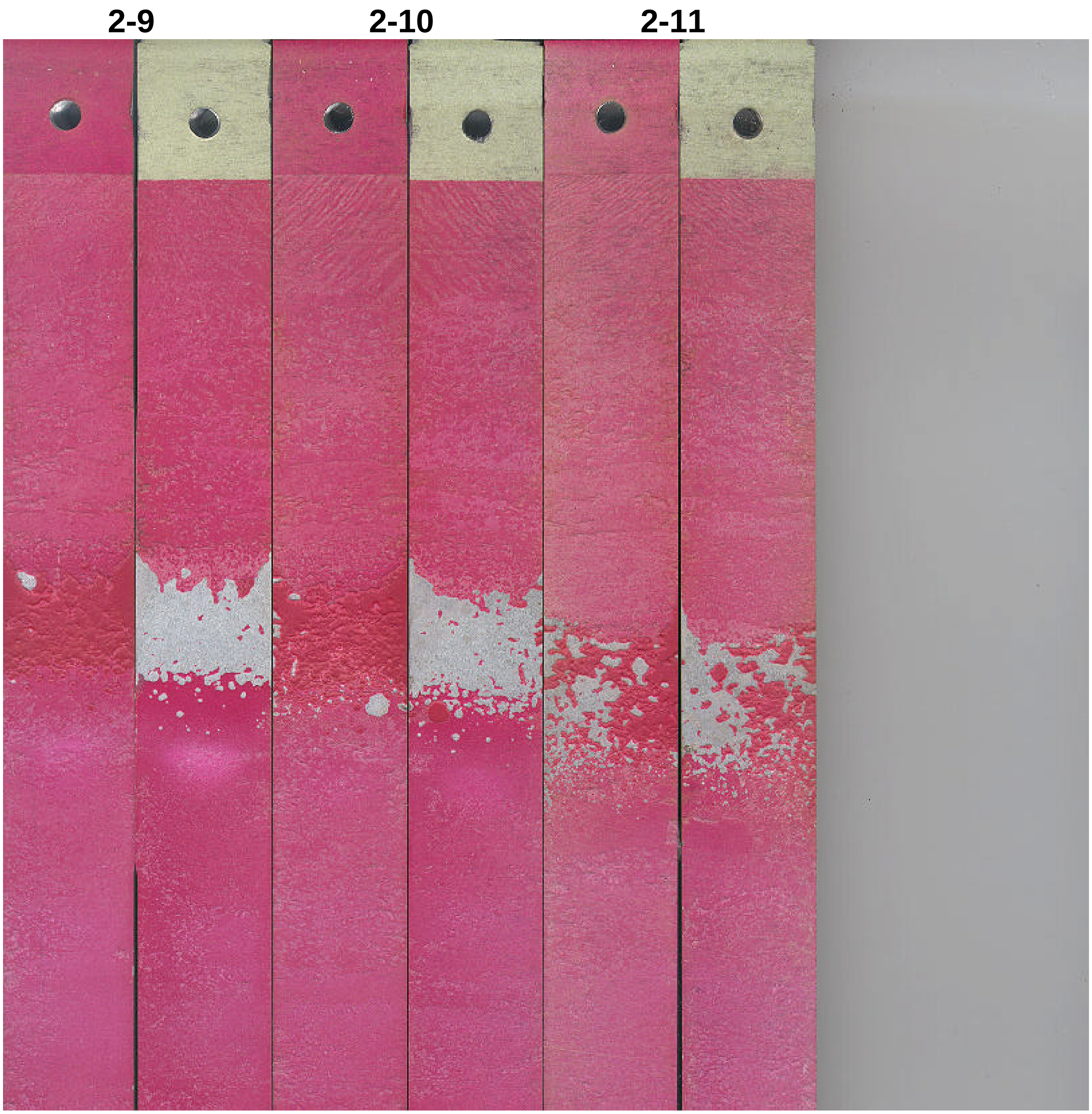
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 2-5 through 2-8 (Merit SK-62-P180)



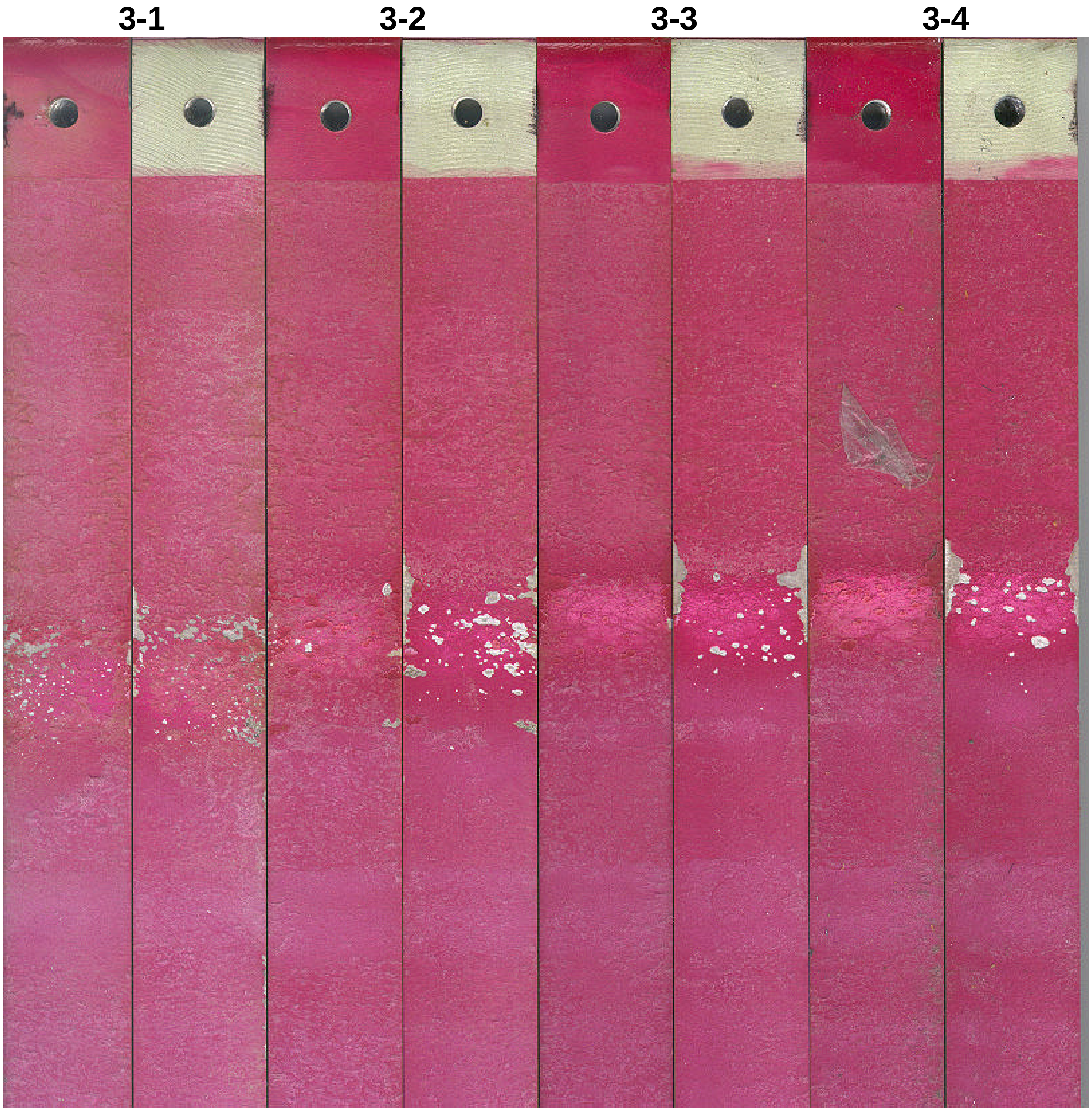
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 2-9 through 2-11 (Merit SK-62-P180)



Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

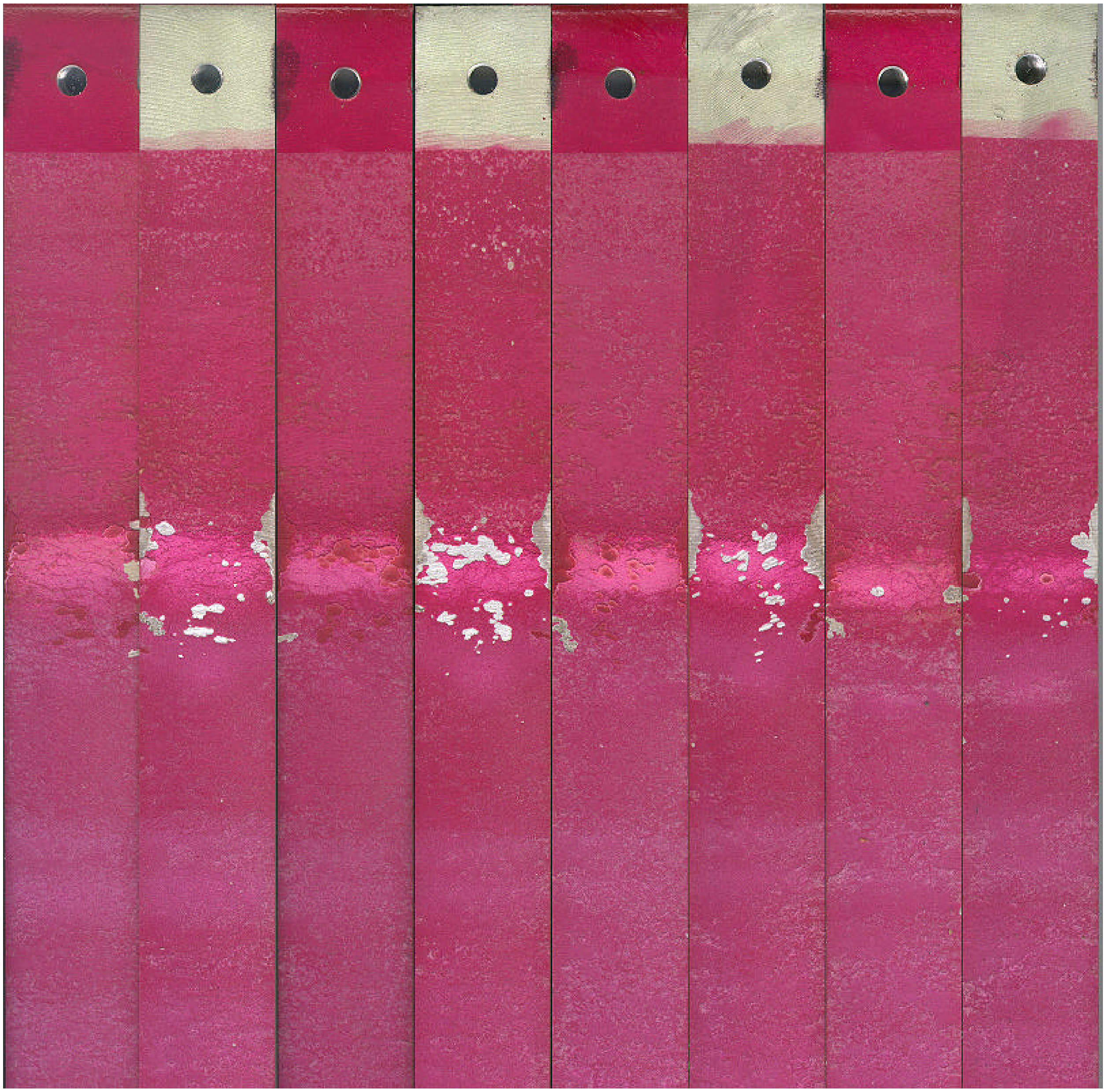
Samples 3-1 through 3-4 (Merit Zirc-Plus 120)



Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

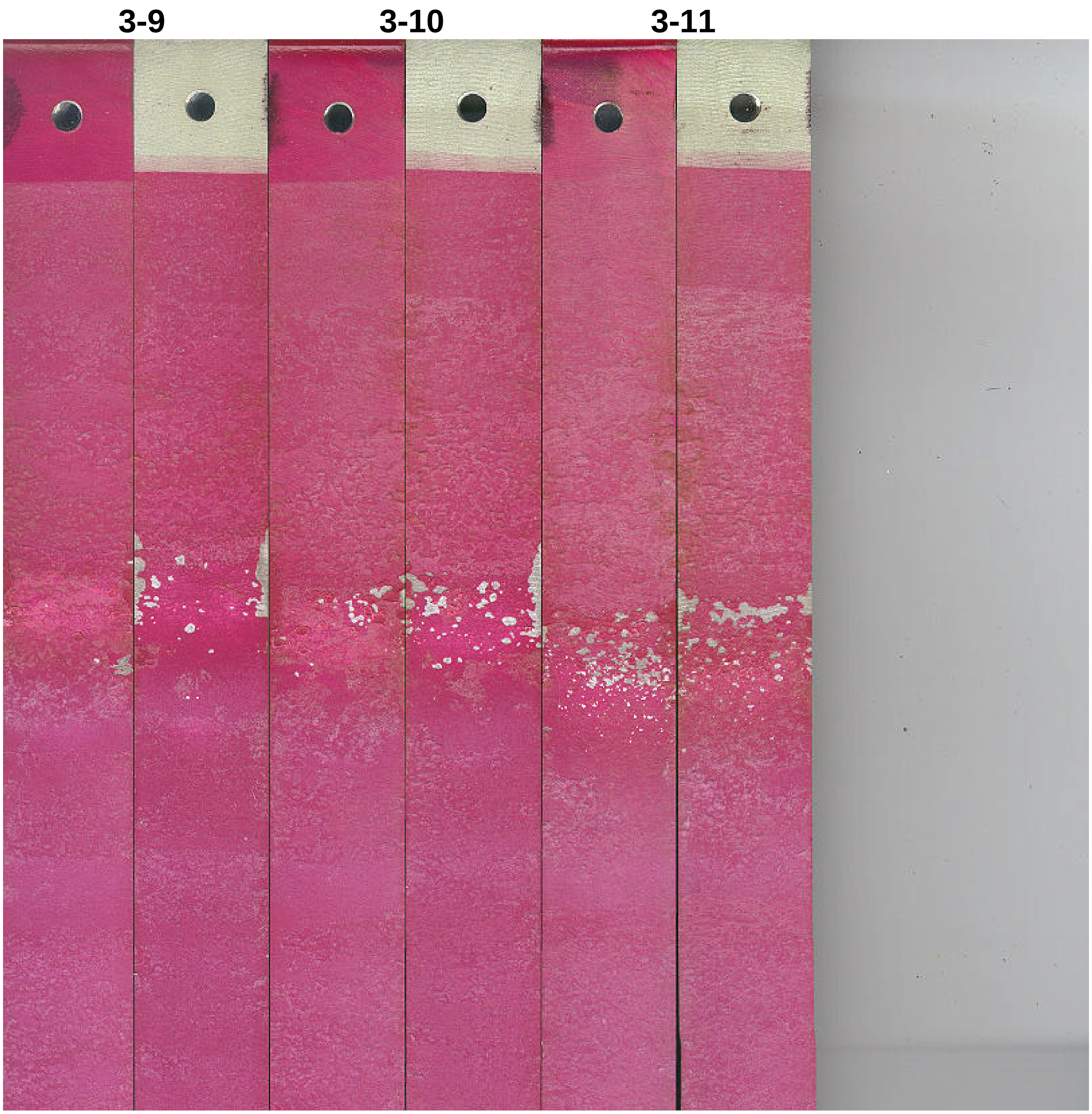
Samples 3-5 through 3-8 (Merit Zirc-Plus 120)

3-5	3-6	3-7	3-8



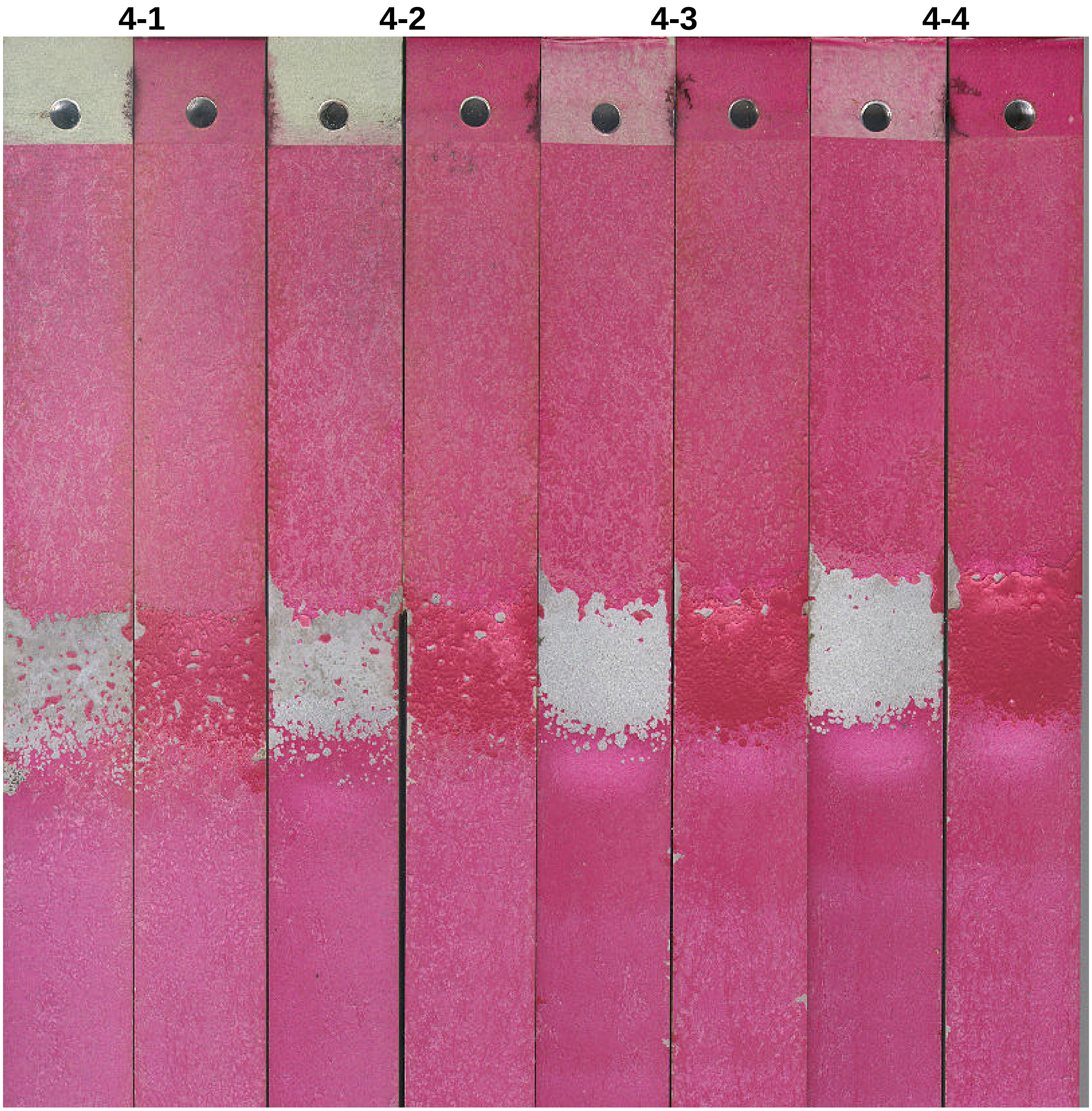
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 3-9 through 3-11 (Merit Zirc-Plus 120)



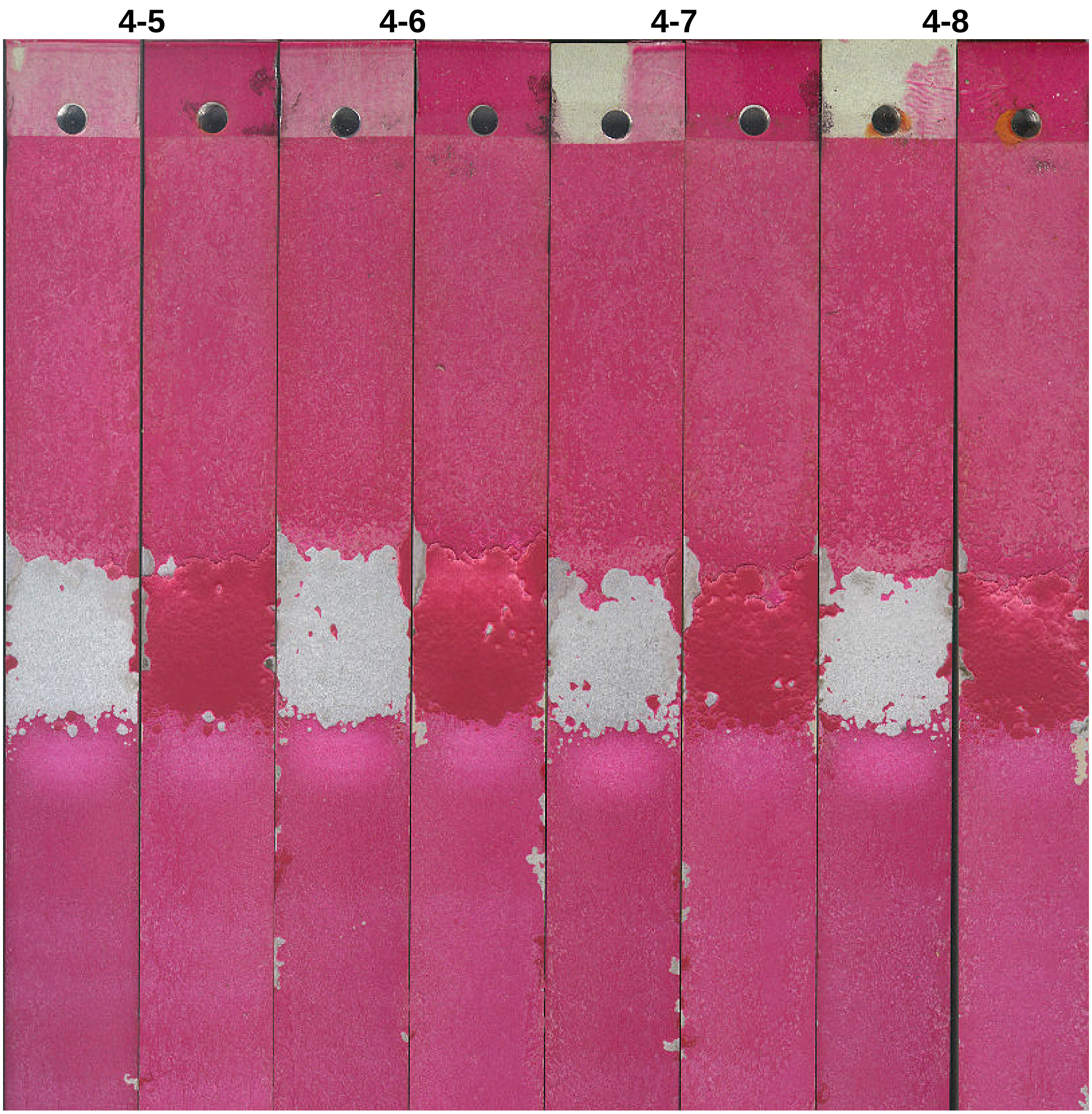
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 4-1 through 4-4 (3M 268L 80 micron)



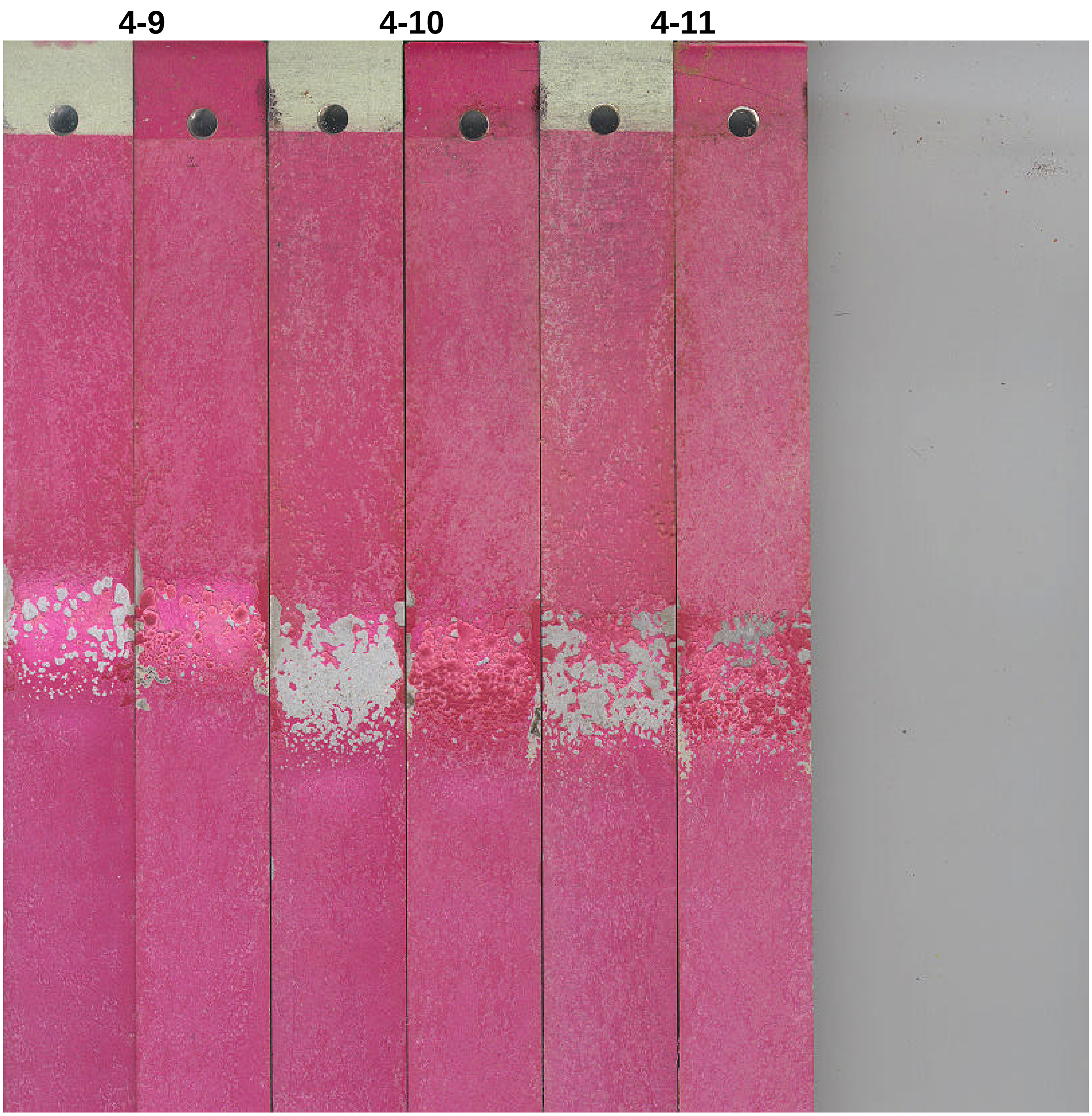
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 4-5 through 4-8 (3M 268L 80 micron)



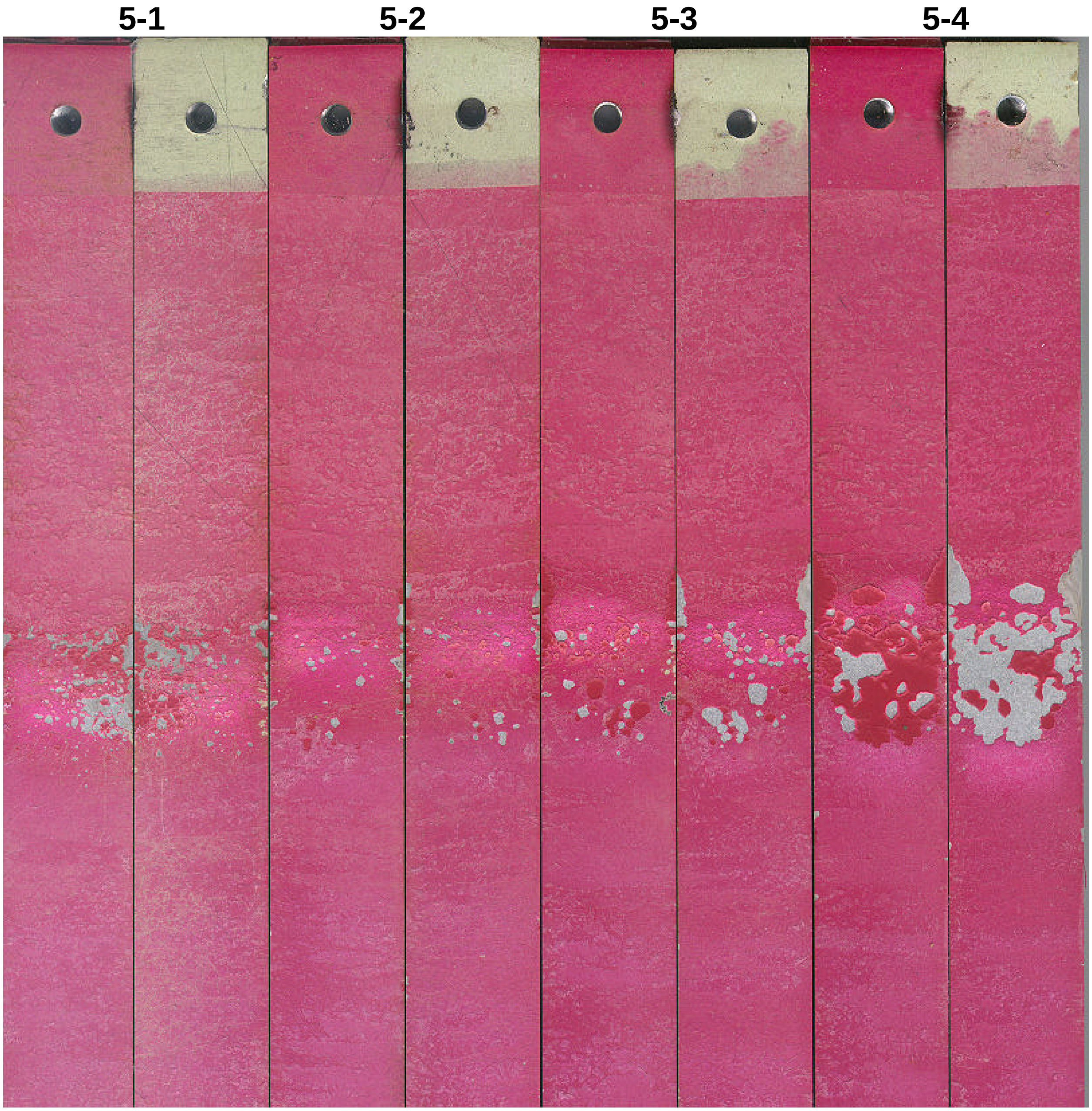
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 4-9 through 4-11 (3M 268L 80 micron)



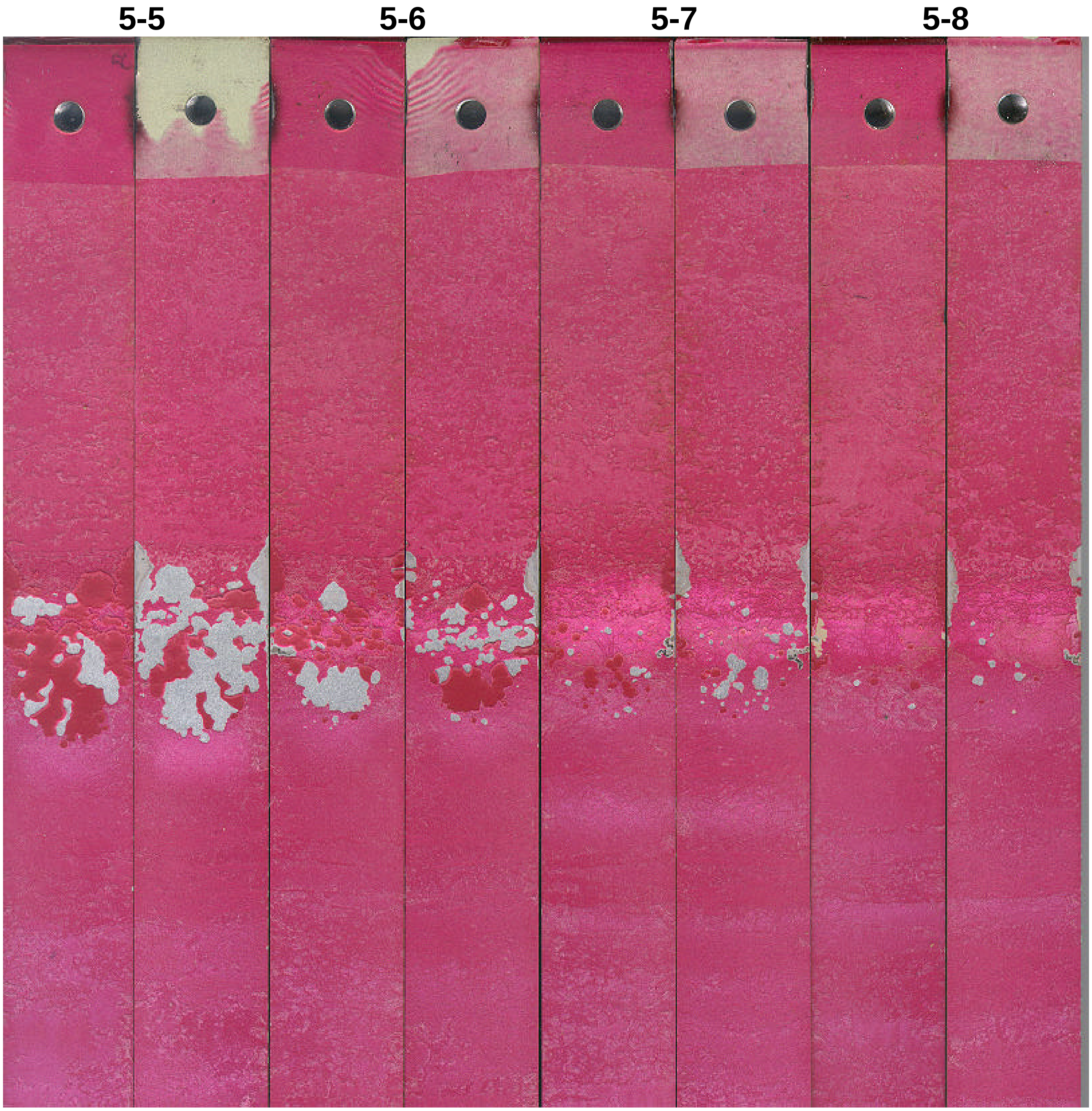
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 5-1 through 5-4 (3M 326U #220 alumina)



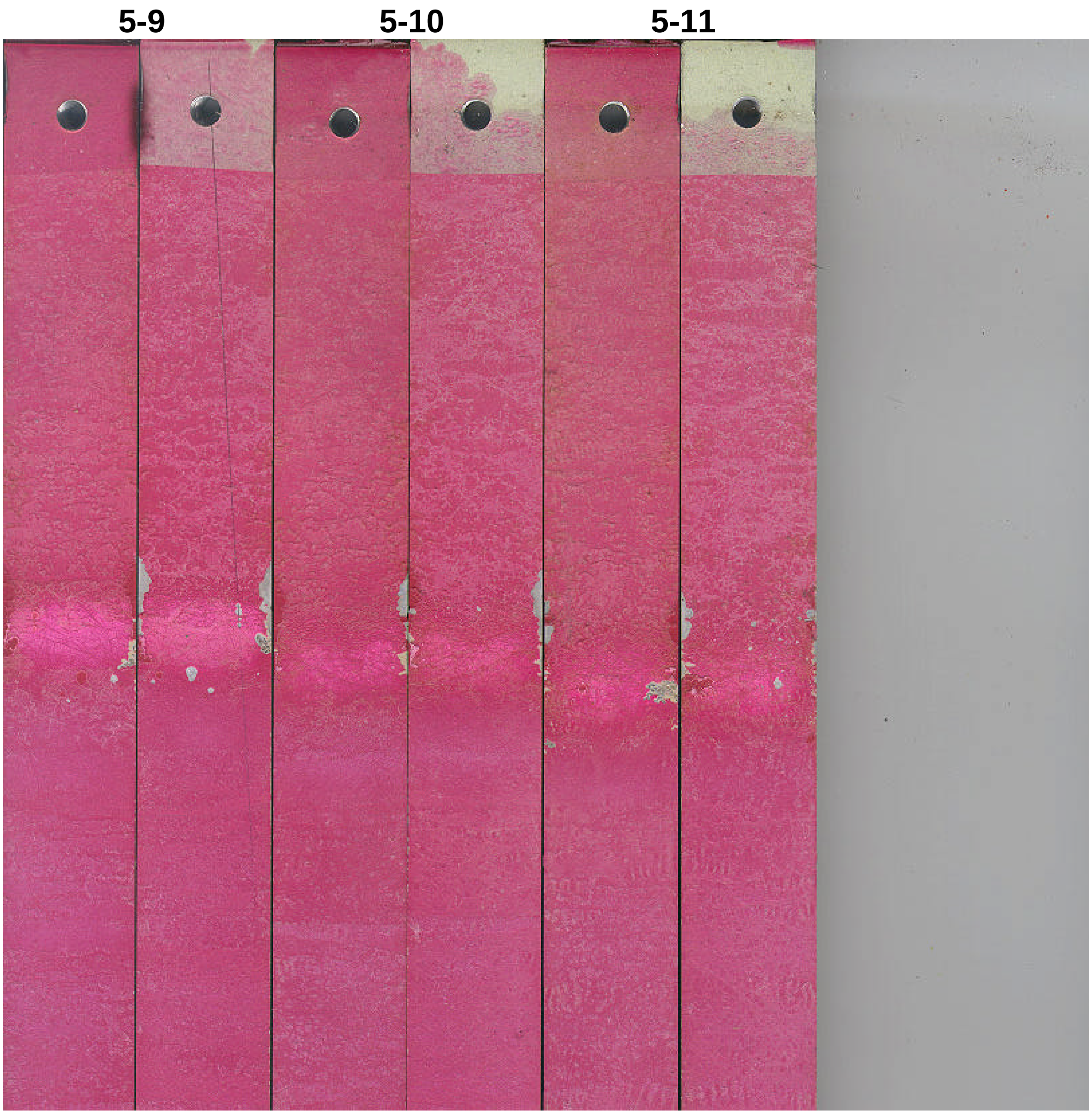
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 5-5 through 5-8 (3M 326U #220 alumina)



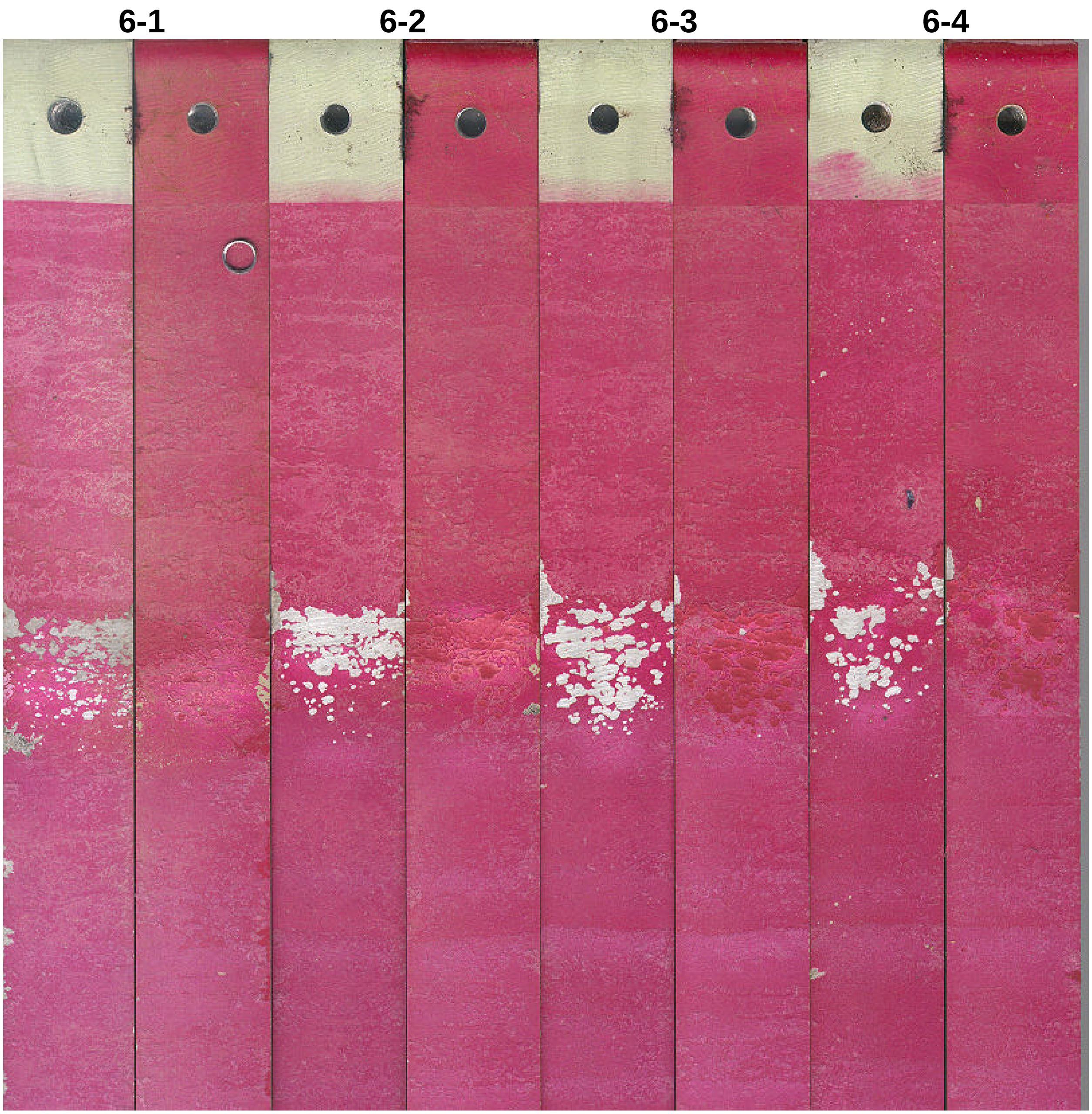
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 5-9 through 5-11 (3M 326U #220 alumina)



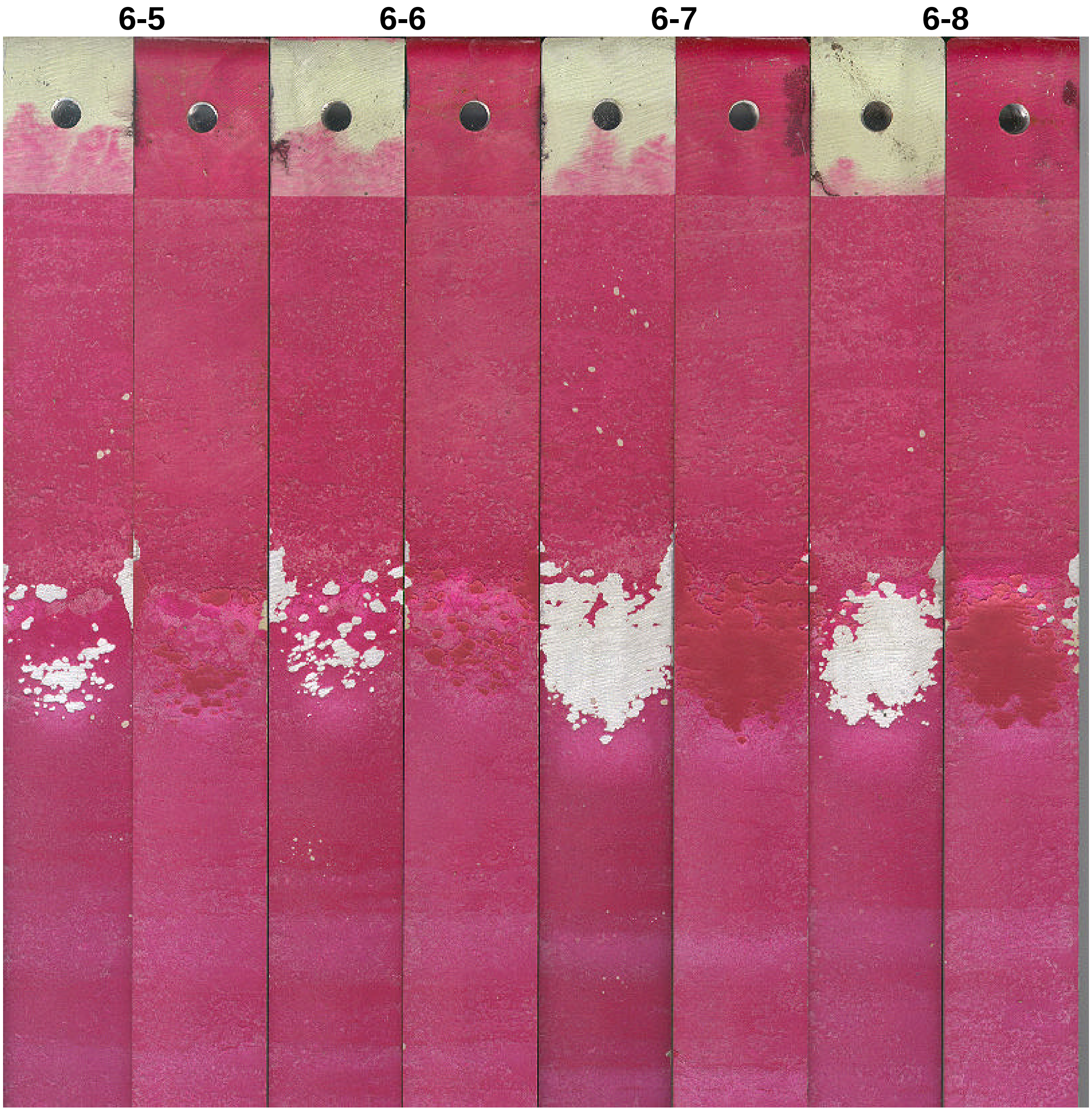
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 6-1 through 6-4 (StAb A/O Xtra #120 grit)



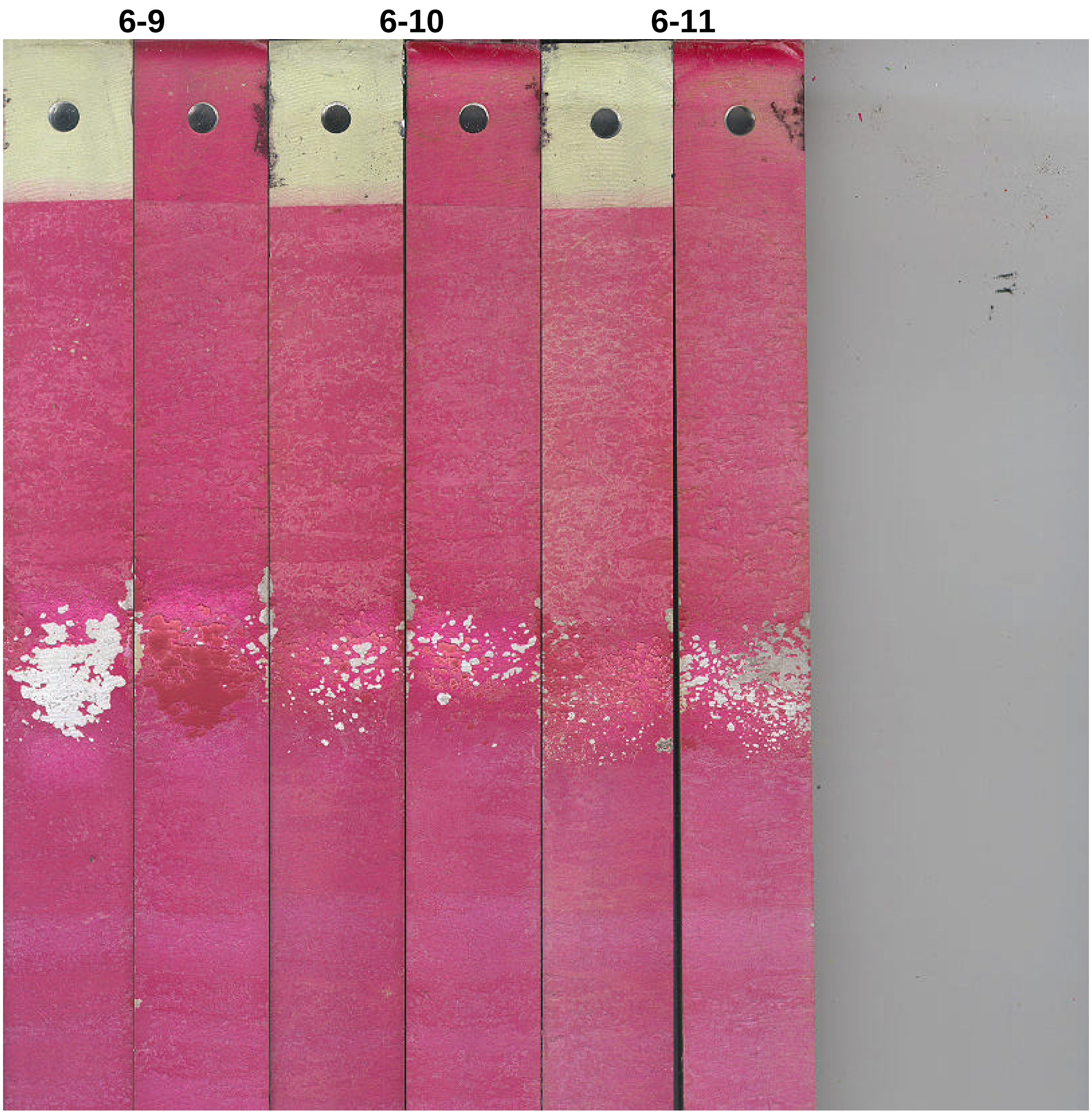
Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 6-5 through 6-8 (StAb A/O Xtra #120 grit)



Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 6-9 through 6-11 (StAb A/O Xtra #120 grit)



Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

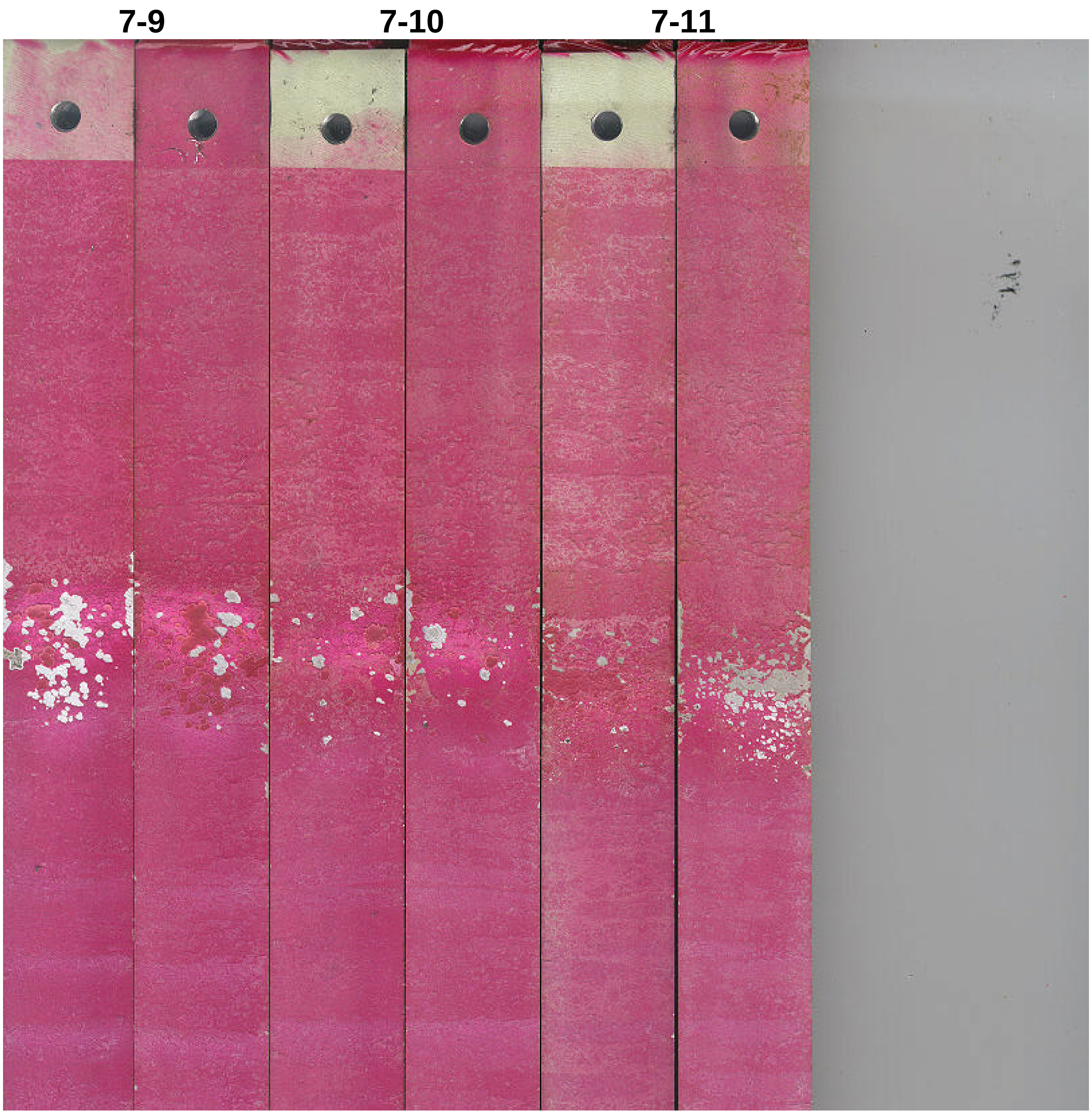
Samples 7-1 through 7-4 (Scotch-Brite™ med. Roloc)

Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 7-5 through 7-8 (Scotch-Brite™ med. Roloc)

Systematic Abrasive Media Study - Double Cantilever Beam Specimens (Section 4.3.3)

Samples 7-9 through 7-11 (Scotch-Brite™ med. Roloc)



ESCA Data for Al substrate controls, Al substrates deoxidized with 3M 210U P180 sandpaper, and 3M 210U P180 sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			3M 210U-P180 Al substrate			3M 210U-P180 sandpaper	
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**as received**	**after use**
Atomic %:											
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	16.6%	17.5%	14.5%	60.8%	58.4%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	45.8%	44.8%	44.5%	16.2%	17.4%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	33.7%	35.4%	38.0%	*	0.7%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	2.6%	0.8%	1.9%	*	*
Copper	0.4%	0.4%	0.2%	*	*	*	*	0.1%	*	*	*
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	*	*	*	*
Chlorine	*	*	*	*	0.7%	*	*	*	*	0.4%	0.5%
Nitrogen	*	*	*	*	*	*	*	*	*	22.6%	23.1%
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*	*	*
Calcium	*	*	*	*	*	*	*	*	*	*	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*	*	*
Sulfur	*	*	*	*	*	*	1.3%	1.5%	1.2%	*	*
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls, Al substrates deoxidized with Merit SK-62-P180 sandpaper, and Merit SK-62-P180 sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			Merit SK-62-P180 Al substrate			Merit SK-62-P180 sandpaper	
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**as received**	**after use**
Atomic %:											
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	15.4%	14.4%	13.8%	76.9%	75.1%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	45.9%	45.7%	43.6%	17.9%	17.4%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	35.1%	36.5%	38.8%	*	0.4%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	1.9%	1.1%	3.1%	*	1.8%
Copper	0.4%	0.4%	0.2%	*	*	*	*	0.1%	0.1%	*	*
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	0.4%	*	*	0.8%
Chlorine	*	*	*	*	0.7%	*	*	*	*	0.5%	0.4%
Nitrogen	*	*	*	*	*	*	*	*	*	2.9%	2.5%
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*	0.7%	1.0%
Calcium	*	*	*	*	*	*	*	*	*	0.2%	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*	0.9%	0.6%
Sulfur	*	*	*	*	*	*	1.7%	1.9%	0.7%	*	*
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls and Al substrates deoxidized with Merit Zirc-Plus 120 sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			Merit 120 Zr+ Al substrate		
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**
Atomic %:									
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	15.0%	12.5%	11.4%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	43.7%	44.5%	42.8%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	35.9%	39.2%	40.4%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	2.6%	1.5%	3.1%
Copper	0.4%	0.4%	0.2%	*	*	*	0.2%	0.2%	0.2%
Fluorine	4.8%	5.4%	4.7%	*	*	*	0.7%	1.0%	1.0%
Chlorine	*	*	*	*	0.7%	*	*	*	*
Nitrogen	*	*	*	*	*	*	*	*	*
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*
Calcium	*	*	*	*	*	*	*	*	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*
Sulfur	*	*	*	*	*	*	1.9%	1.2%	1.2%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls and Al substrates deoxidized with 3M 268L 80 micron sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			268L 80um 5" disc TypeD Al substrate		
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**
Atomic %:									
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	17.7%	14.6%	14.6%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	45.0%	44.6%	44.3%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	33.7%	37.4%	38.9%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	2.8%	2.5%	2.0%
Copper	0.4%	0.4%	0.2%	*	*	*	*	0.1%	*
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	*	*
Chlorine	*	*	*	*	0.7%	*	*	*	*
Nitrogen	*	*	*	*	*	*	*	*	*
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*
Calcium	*	*	*	*	*	*	*	*	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*
Sulfur	*	*	*	*	*	*	0.9%	0.8%	0.3%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls and Al substrates deoxidized with 3M 268L 80 micron sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			3M 326U #220 alumina Al substrate		
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**
Atomic %:									
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	15.0%	13.2%	12.7%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	45.7%	44.6%	44.2%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	35.2%	38.6%	38.6%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	2.3%	1.9%	3.1%
Copper	0.4%	0.4%	0.2%	*	*	*	0.1%	0.2%	0.2%
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	*	*
Chlorine	*	*	*	*	0.7%	*	*	*	*
Nitrogen	*	*	*	*	*	*	*	*	*
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*
Calcium	*	*	*	*	*	*	*	*	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*
Sulfur	*	*	*	*	*	*	1.8%	1.6%	1.1%
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls, Al substrates deoxidized with StAb A/O Xtra #120 grit sandpaper, and StAb A/O Xtra #120 grit sandpaper

	chemically deoxed Al substrate			solvent wiped Al substrate			StAb A/O Xtra #120 Al substrate			StAb A/O Xtra #120 sandpaper	
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**as received**	**after use**
Atomic %:											
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	15.4%	13.5%	12.8%	79.9%	77.1%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	43.9%	44.1%	44.2%	14.2%	15.0%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	35.9%	39.5%	39.1%	*	1.4%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	3.3%	1.2%	3.0%	*	*
Copper	0.4%	0.4%	0.2%	*	*	*	0.1%	0.2%	0.2%	*	*
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	*	*	0.3%	1.1%
Chlorine	*	*	*	*	0.7%	*	*	*	*	3.7%	3.7%
Nitrogen	*	*	*	*	*	*	*	*	*	*	*
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*	1.4%	1.4%
Calcium	*	*	*	*	*	*	*	*	*	0.4%	0.3%
Silicon	4.2%	*	4.2%	*	*	*	*	*	*	*	*
Sulfur	*	*	*	*	*	*	1.3%	1.5%	0.9%	*	*
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%

ESCA Data for Al substrate controls, Al substrates deoxidized with Scotch-Brite™ med. Roloc disc (maroon) media, and Scotch-Brite™ med. Roloc disc (maroon) media

	chemically deoxed Al substrate			solvent wiped Al substrate			Scotch-Brite med. roloc Al substrate			Scotch-Brite med. roloc media	
	area 1	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**area 1**	**area 2**	**area 3**	**as received**	**after use**
Atomic %:											
Carbon	26.2%	24.0%	27.2%	36.7%	37.1%	34.5%	26.6%	31.3%	29.7%	93.3%	94.1%
Oxygen	36.6%	37.3%	34.8%	34.1%	33.4%	35.2%	38.8%	33.5%	34.7%	4.4%	4.5%
Aluminum	24.0%	26.9%	23.8%	6.2%	6.6%	5.9%	33.0%	31.8%	34.1%	*	0.6%
Magnesium	*	1.0%	0.8%	23.0%	22.2%	24.4%	0.5%	1.4%	0.5%	*	*
Copper	0.4%	0.4%	0.2%	*	*	*	0.1%	0.2%	0.1%	*	*
Fluorine	4.8%	5.4%	4.7%	*	*	*	*	*	*	*	*
Chlorine	*	*	*	*	0.7%	*	*	*	*	*	*
Nitrogen	*	*	*	*	*	*	0.6%	0.6%	0.3%	*	*
Chrome	3.0%	3.8%	3.2%	*	*	*	*	*	*	*	*
Sodium	0.9%	1.3%	1.0%	*	*	*	*	*	*	0.4%	0.3%
Calcium	*	*	*	*	*	*	*	*	*	*	*
Silicon	4.2%	*	4.2%	*	*	*	*	*	*	2.0%	0.5%
Sulfur	*	*	*	*	*	*	0.4%	1.3%	0.7%	*	*
	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%	100.0%